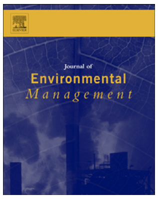
Journal of Environmental Management 191 (2017) 35–57

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman



Review

An update on synthetic dyes adsorption onto clay based minerals: A state-of-art review

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ARTICLE INFO

Article history:
Received 20 September 2016
Received in revised form
8 December 2016
Accepted 12 December 2016

Keywords:
Clays
Dyes
Wastewater
Adsorption capacity and mechanisms

ABSTRACT

Dyes are growing to be a problematic class of pollutants to the environment. The disposal of dyes in water resources has bad aesthetic and health effects, hence the need to remove them from the environment. The need for treatment methods that are effective and low in price is rising hence a lot of research interest is being diverted towards adsorbents that are cheap, preferable naturally occurring materials like clays. In most reported dye adsorption studies, limited information on the relationship between characterization results with adsorbent performance on dye removal has been given. This review article seeks to report on the link between the adsorption characteristics of the clays and their adsorption capacities and to gather information on the modifications done on clays to improve their adsorption capacities. A critical analysis of the different mechanisms involved during the decolouration process and their application for dye removal has been discussed in detail in this up-to-date review. From a wide range of consulted literature review, it is evident that some clays have appreciable adsorption capacities on top of being widely available. It was also noted that several parameters like contact time, dosage, concentration, temperature and pH affect the removal of dyes. Furthermore, the application of clay minerals for decolourising water represents economic viable and locally available materials that can be used substantially for pollution control and management. Conclusions were also drawn and suggestions for future research perspectives are proposed.

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http://dx.doi.org/10.1016/j.jenvman.2016.12.031
0301-4797/

1. Introduction

Different classes of dyes are used in numerous industries including rubber, textiles, cosmetics, plastics, leather, food and paper making. The variability of these dyes is seen in wastewaters discharged from these industries. “Generally dyes are stable to light, heat and oxidizing agents and are usually non-biodegradable” (Kono, 2015). Because these dyes give colour to the receiving water bodies hence degrading their aesthetic values, it is of paramount importance that their presence in a water body be managed (Kant, 2012).

The presence of colour in an aquatic ecosystem reduces the penetration of sunlight to benthic organisms thus limiting the process of photosynthesis. Dyes also affect the aesthetic value of an aquatic ecosystem due to colouration of water resources (Yagub et al., 2014). The key concern in the treatment of wastewater is the release of dyes and their metabolites into the environment, as some may be mutagens and carcinogens. Some of these dyes are xenobiotic in nature and aerobically recalcitrant to biodegradation (Gupta et al., 2013) and thus pose a threat when wastewater is disposed off to the adjacent environment without being treated. In that regard, there is a need to find treatment technologies that can decolourise the water and at the same time reduce the toxic effects of the dyes to within the recommended water quality guidelines.

Being among the most demanding environmental tasks of the modern day, the increasing amount of toxic industrial waste has led to the development of various methods for its eradication and removal from wastewaters (Chollom, 2014). Usually industrial effluents are treated by several methods including chemical degradation, advanced oxidation processes, adsorption, precipitation, biodegradation and chemical coagulation (Pajootan et al., 2012). These methods have been extensively applied, however they have some shortcomings (Kobya et al., 2007; Mohan et al., 2007). For instance, a lot of time is needed for the biological methods and more often than not, the biological methods are less effective when it comes to highly structured polymer dyes. Buthelezi et al. (2012) reported that dyes are non-biodegradable by nature, as such, biological methods will be inapplicable and their applicability is limited to few dyes because many dyes in the market are toxic to the organisms used hence the biological methods cannot be applied to treat those dyed wastewaters.

Chemical coagulation processes produce huge amounts of sludge thereby causing a lot of pollution as a result of the different chemical reactions that would have taken place during the wastewater treatment processes (Balik and Aydin, 2016). Merzouk et al. (2011) reported that the most effective and important treatment method is chemical degradation using oxidative agents like chlorine, however the disadvantage of this method is the production of highly toxic products like organochlorine compounds. Amongst other oxidation processes, there are more advanced processes not limited to some of the following: fenton reactive and ultrasonic oxidation, UV and ozone–UV combined oxidation and photocatalysis. These oxidation processes are said to be not economically feasible (Daneshvar et al., 2006). The great variability of the wastewater composition often leads to inefficiencies or inadequate treatment of the dye effluents (Drouiche et al., 2011). Having pointed out the above, adsorptions seems to be among the most favoured wastewater treatment technique because of its environmental and economic sustainability.

2. Dyes

Dyes can be defined as organic compounds that have colour and are used to give colour to different substrates like cosmetics, paper, drugs, leather, fur, greases hair, waxes, plastics and textile materials. “Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart colour” (Yagub et al., 2014). Dyes can be classified according to where they are derived. They can be from natural or synthetic sources. Natural dyes are extracted from sources including plants, animals and minerals. Natural dyes were used mostly during early textile industry and these include Jackfruit, Onion, eucalyptus, Turmeric, Weld and henna (Dawood and Sen, 2014). However, because of population increase and industrial activities, people are moving away from natural dyes because they are failing to meet the industrial demand hence their application nowadays is mostly found in the food industry. Synthetic dyes have replaced natural dyes almost completely particularly in the fabrics and textile industry. Several types of dyes are used in numerous industries and these include basic, acid, reactive, direct, vat and disperse dyes (Chen et al., 2016). All these dyes are soluble in water except for disperse and vat dyes. Dyes also contain traces of metals like chromium, copper, lead, zinc, and cobalt apart from vat and disperse dyes. Dye effluents from industries are known for their organic content, high colour and are harmful as well (Gupta et al., 2013).

2.1. *Physico-chemical properties of dyes*

Normally dyes are soluble in water or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance (Hunger, 2003). Molecules of dyes are chemically bonded to the surface and after application to a material they become a part of it. For dyes to be marketable in the commercial industry, they should have high colour intensity and the colour must not fade away with time. The intensity of the colour depends on how strongly it absorbs radiation in the visible region (Zollinger, 1987). The structures in dyes that give colour (unsaturated groups that can undergo π-π and n-π transitions) are called chromophores (see Figs. 1 and 2):

There is also another group of structures that cause colour intensification and these structures are called auxochromes. Unlike chromophores, auxochromes cannot undergo π-π transitions, but instead can undergo n electrons transition. The following are examples of chromophores: −OH, −OR, $-NH_2$, −NHR, −NR2 and −X.

3. Dye effluent treatment methods

Several technologies to treat dye wastewater have been developed and these include coagulation, adsorption, membrane separation process, precipitation, electrochemical, chemical oxidation and biological processes (Yagub et al., 2014). The several methods mentioned however can be divided into three major types which are: biological, chemical and physical and their major strengths and weaknesses are shown in Table 1.

The biodegradation of synthetic dyes by microorganisms is a common and simple method of wastewater treatment by operation but the processes involved in the biological degradation can be complex. A number of microorganisms have been used for the decolouration of dyes. These methods of biological treatment include colour removal by *Sphingomonas*, white rot fungi, pseudomonas strains, and microbial cultures, under aerobic and anaerobic or mixed conditions as well as adsorption using living and dead biomass (Adensola et al., 2016; Babarinde and Onyiaocha, 2016; Tahir et al., 2016). Most of these dye compounds are however very stable and resistant to biological degradation. The isolation of new strains or the adaptation of existing ones to the decomposition of dyes will probably increase the efficacy of bioremediation of dyes in the near future. The biodegradation of dye effluents by the use of microorganisms is an acceptable and easy method by operation (Buthelezi et al., 2012).

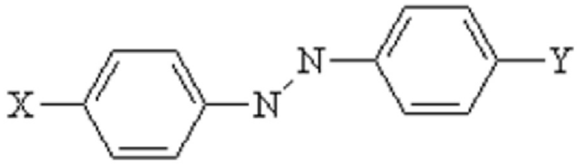
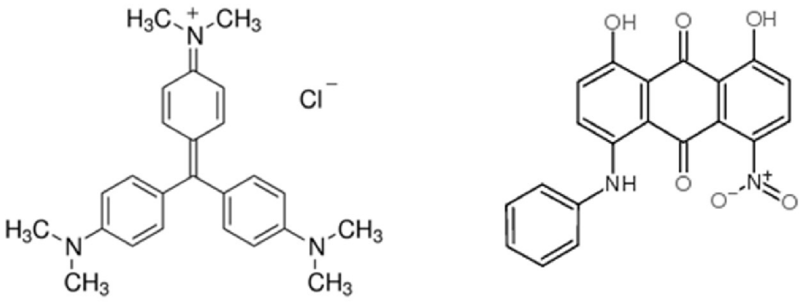


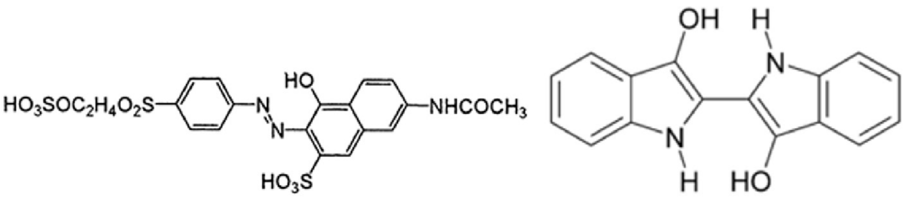
Fig. 2. Example of a chromophores.

Chemical wastewater treatment methods include precipitation, flocculation, coagulation, flotation and filtration, electrokinetic coagulation, oxidation methods, electroflotation, irradiation or electrochemical processes (Pajootan et al., 2012). The effectiveness of chemical methods depends on the interaction between the contaminants in the wastewater and the nature of chemical used (Iqbal et al., 2014). The chemicals treat the wastewater by way of either assisting in the separation process or helping to ruin and neutralise some of the detrimental effects caused by the pollutants (Mohan et al., 2007). These techniques are good at decolorizing water but at the same time are expensive and disadvantageous because they create a lot of sludge after use and therefore lead to a sludge disposal problem (Kobya et al., 2007). Moreover, secondary pollution problem can arise because of too much chemical use. Oxidation processes generate powerful oxidizing agents like as hydroxyl radicals and these have been used successfully for



Crystal violet

Disperse blue 18



Reactive orange 15

Synthetic indigo

Fig. 1. The chemical structures of some synthetic dyes (Hunger, 2003).

Table 1
The pros and cons of wastewater treatment methods (Robinson et al., 2001).

Treatment Method	Pros	Cons
Ion-exchange	Adsorbent can be regenerated and therefore used for several times	Only effective for certain types of dyes.
Membrane processes	Reuse of water salts and heat	Handling and disposal of concentrate stream, flux decline
Electrochemical processes	Breakdown compounds and are non-hazardous	Economically less feasible because high electricity costs
Photochemical	No sludge production	Formation of by products
Ozonation processes	Applied in gaseous state: no modification of volume	Ozonation processes have a very short half-life
Coagulation/flocculation	Insoluble dyes can be removed and it is economically feasible	The amount of sludge produced is high.

degrading pollutants but they are also very expensive and commercially unattractive because of high consumption of chemicals and electrical energy demand (Bilal et al., 2014; Jamal et al., 2015; Qureshi et al., 2015).

Physical methods are also extensive and these include adsorption techniques, reverse osmosis, electrodialysis, membrane-filtration processes and nanofiltration (Khan et al., 2015; Shon et al., 2013). The main drawback of the membrane processes is the short period of use before the membrane starts fouling and the various costs coming as a result of constant replacement of the membranes eventually leading to membrane processes being economically unviable (Shamraiz et al., 2016). According to documented studies, adsorption is one of the most widespread wastewater treatment approach that has been proven effective and efficient in depollution science since it can remove contaminants and decolour the water resources (Gomes et al., 2015; Mu and Wang, 2016; Tahir et al., 2016; Srinivasan, 2011). If a treatment plant is given a proper adsorption process design, it produces a high quality treated effluent. Adsorption processes offer an attractive alternative treatment method for contaminated waters, particularly in cases where the adsorbent is inexpensive, locally available, abundant and requires less additional pre-treatment step before it is used (Crini, 2006).

Although, the adsorption process has been deemed to offer an attractive alternative treatment technology for polluted waters, it also has its drawbacks. Adsorption is known to produce highly concentrated sludge that lead to a problem of sludge disposal. It has also been reported to be less effective for some dyes, especially the highly concentrated dyes. Moreover it can be very expensive when using high cost adsorbents like activated carbon which are also costly to regenerate. A number of investigations have shown that several factors affect the adsorption process but worth to note is that adsorption is vastly dependent on the pH media, basically meaning that to attain maximum adsorption capacities, the pH has to be adjusted in most cases. Besides that, the physical and chemical characteristics of the adsorbent can have an intense influence on the capacity and rate of the adsorption process. e.g low surface area for some adsorbents leads to low adsorption capacity (Benefield et al., 1982).

4. The adsorption process

Oremusová (2007) defines adsorption as "a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate)". Generally, the adsorbent has a fixed total uptake, where a particular solute is replaced by another for example, in ion exchange processes. When an adsorbent is contacted with liquid containing an absorbable solute, adsorption occurs until equilibrium is achieved or when the surface of an adsorbent is saturated with an adsorbate (Kalibantonga, 2004).

The adsorption process can be divided into two main types, namely, physical and chemical both sometimes referred to as physiosorption and chemisorption respectively. The difference between the two types of adsorption is that, in physical adsorption the adsorbate sticks to the surface through weak intermolecular interactions like such as Van der Waals forces, hydrophobicity, hydrogen bonding, polarity, static interactions, dipole–dipole interactions and Π- Π interactions (Dawood and Sen, 2014). On the other hand, in chemisorption, molecules stick to the surface by forming a chemical bond through electron exchange (Artioli, 2008). Some of the differences between physiosorption and chemisorption are shown in Table 2.

In adsorption processes, the contaminated water is passed through a sorbent bed. The adsorbent material will retain the contaminants by either chemical, physical or ion exchange mechanisms. After a certain period of time of operation, the adsorbent gets saturated and will require regeneration/replacement depending on regeneration feasibility (Chapman and Siebold, 1912).

Worch (2012) pointed out that the extent of adsorption is directly proportional to the specific area of the adsorbent. The specific area is that part of the entire area available for adsorption. It is related to the grain size of the adsorbent. The choice of particle size is made by considering the following factors:

- ❖ the ease of mass transfer from the fluid to the surface,
- ❖ creation of as much interfacial surface area as possible and reduction of antiparticle diffusion path length, all of which favor smaller particles
- ❖ maintenance of a low pressure drop, which favors larger particles (Worch, 2012).

For an adsorbent to be selected as favorable, a number of factors are looked at. These include ease of operation, cost of the medium, adsorption capacity, potential for reuse and likelihood of regeneration (Worch, 2012). Various naturally occurring materials that are both readily available and abundant have been explored as adsorbents for the removal of dyes from wastewater (Ghosh and Reddy, 2014; Ali et al., 2012; Tehrani-Bagha et al., 2011; Rafatullah et al., 2010). A great interest has grown towards naturally occurring adsorbents, preferably developing sorbents that have a high adsorption capacity and has low cost for removing pollutants from contaminated waters. Although a wide variability of sorbents have been used for wastewater treatment, naturally available clays have been the adsorbents of choice in most developing countries (Ali et al., 2012; Hajjaji et al., 2016; Mu and Wang, 2016; Santos and Boaventura, 2016).

5. Clays

"Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides" (Pinnavaia, 1983). Clay materials possess structures that are organized in layers and they are categorized by those different layered structures (Ajbary et al., 2013; Li

Table 2
Comparison between physiosorption and chemisorption (Jaafar, 2006).

Physiosorption	Chemisorption
Weak intermolecular forces like van der Waals forces	Strong covalent bonding involving electron exchange
Low enthalpy: $\Delta H < 20$ kJ/mol	High enthalpy: $\Delta H \sim 400$ kJ/mol
Multilayer adsorption	Monomolecular adsorption
Low temperature, constantly lower than the adsorbate critical temperature	High temperatures
Low activation energy	High activation energy
Reversible	Non-reversible.
Nonselective surface attachment	Selective surface attachment

et al., 2013; Savic et al., 2014). Clay materials fall under various types like pyrophyllite - talc, smectites - montmorillonite, mica - illite, kaolinite, serpentine, vermiculite and sepiolite (Shichi and Takaqi, 2000). Fig. 3 shows the structure of a typical clay.

5.1. *Clays and adsorption: physicochemical characteristics favouring adsorption*

The chemistry which occurs on the surfaces of clay gives them high flexibility in adsorption processes. The surface chemistry involves the structure, ion exchange capacity, specific surface area, mechano-chemical stability, water holding capacity and reactivity of the surface which influences physical and chemical properties of clay minerals (Eren, 2010). Usually, these clay materials are used as natural as they are without being chemically modified. Nonetheless, chemical modification can improve the clay‘s adsorption capacity leading to its widespread use in novel technologies (Liang et al., 2013).

According to Elmoubarki et al. (2015), clay adsorption capacities are usually dependent on the net negative charge found on the clay minerals. The negative charge contributes to the clay's ability to adsorb positively charged ions. Furthermore, clays' adsorption characteristics arise from their large pore sizes and surface area (Yan et al., 2015). Generally, clays have exchangeable ions on their surface (Eren, 2010). This characteristic leads to clays playing a crucial role in the environment by being natural pollutant scavengers by way of cations and anions take up through adsorption and ion exchange. Ions that are usually found on surfaces of the clay include H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+ and Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-. Cation exchange with occurs readily without affecting the clay mineral's structure (Huang et al., 2011).

Clay minerals display a strong attraction to cationic and anionic dyes (Crini, 2006; Hajjaji et al., 2016; Santos et al., 2016; Sarma et al., 2016; Yan et al., 2015; Yu et al., 2015). Nevertheless, the adsorption capability for basic dyes is comparable greater than that of acid dyes as shown in Table 2. From Table 2, it can be seen that the adsorption capacities recorded on basic dye like Methylene Blue and Malachite Green were approximately three times higher than that recorded for acid dyes like Congo Red and Methyl Orange. The main reason behind the differences in adsorption capacities is the charges on the dyes and surface characteristics of clay materials. As stated earlier by Elmoubarki et al. (2015), clay minerals have a net negative charge hence they will strongly attract positively charged basic dyes.

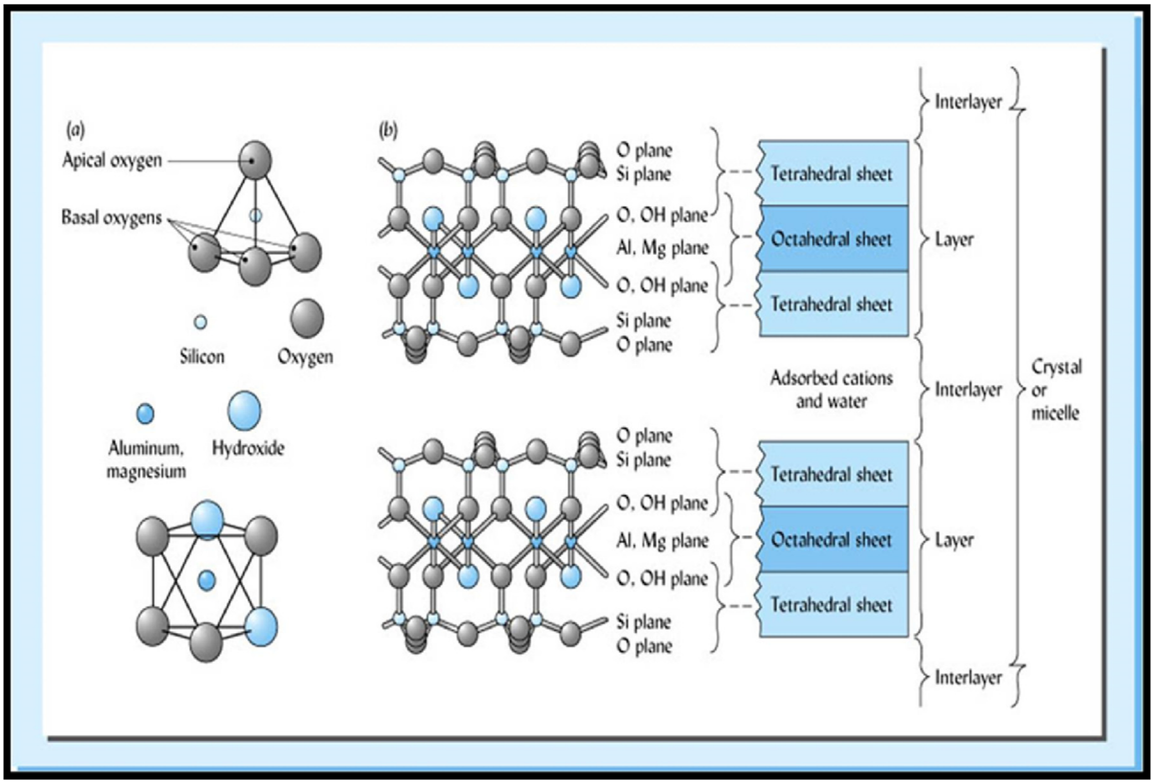


Fig. 3. Structure of a typical clay material (Masindi et al., 2014).

Nonetheless, adsorption capacities can differ even though the dyes have the same charge. Yu et al. (2015) explored the effect of molecular structure on the adsorption of basic dyes, where the adsorption behaviour of methylene blue (MB) and crystal violet (CV) onto natural vermiculite were studied. CV and MB have an ionic charge of +1, so CV was used as a comparative dye, but it has a triangular molecular structure that is considerably different from the molecular structure of MB which is linear. The isotherm modelling results indicated that MB's equilibrium adsorption capacity at 25 °C decreased from 0.076 to 0.053 mmol/g with increase in initial dye concentration from 0.3 to 0.5 mmol/L. A similar phenomenon was observed by Almeida et al. (2009). Results of this study demonstrate that even though dyes have the same charge, their molecular structure can also play a vital role in the adsorption processes. The decrease of MB's adsorption at high initial concentrations could be due to its molecular structure. The linear structure of MB might have had a steric effect on the adsorbate – adsorbate medium more than that of CV causing an equilibrium adsorption density decrease (Yu et al., 2015).

It is also important to note that, is not always the case that clays have a higher adsorption capacity towards basic dyes than acid dyes. This generalisation is made solely depending on the net negative charges of clays but there are instances where clays soils exhibited a much higher adsorption capacity towards acid dyes compared to basic dyes. Santos and Boaventura (2016) reported on the removal of a basic and acid dye on sepiolite clay and their results showed the amount of dye adsorbed was higher for the acid dye than that of the basic day. They investigated the removal of Basic Red 46 (BR) and Direct Blue 85 (DB) and the obtained maximum adsorption capacities at 25 °C and pH 9, were 110 and 232 mg/g, respectively. Ideally, it would be expected that the results show a vice versa trend because of the nature of clays. The authors explained these results in terms of other variables that can affect dye adsorption like temperature and pH. They reported that, in the case of basic red adsorption, the increase in temperature and pH favoured the adsorption extent (from 25 to 35 °C). Regarding the direct blue dye, the adsorption was not influenced by temperature (15–35 °C), but a significant effect of pH was observed, with a sharp decrease in the uptake capacity for strong alkaline conditions. The main reason why sepiolite clay showed a tendency to adsorb acidic dyes than basic dyes was explained in terms of sepiolite's point of zero net proton charge (PZNPC) (Santos and Boaventura, 2016). To estimate the ranges where the clay surface charge is positive or negative, usually the pH of zero charge is determined using electrolytes of different concentrations. When a common intersection point is obtained for the curves resulting from different electrolyte concentrations, the intersection point is not dependent on the ionic concentration and it can be designated as a zero point of charge. The results for sepiolite however showed three distinct intersection points which are referred to as the PZNPC rather than one intersection for PZC. This observation is due to the dual nature of surface charge in minerals, where two different surface charges are present: a permanent negative charge (resulting from the structural isomorphous substitutions) and a pH-dependent charge (primarily related to the dissociation of hydroxyl groups). The high PZNPC values allow to predict a higher propensity of sepiolite to adsorb the anionic dye in pH conditions up to 10. The different pH effects observed for BR (cationic) and DB (anionic) have been also reported for other cationic (Han et al., 2014) and anionic species (Han et al., 2014; Tabak et al., 2009; Tümsek and Avci, 2013).

Many studies have been done using several type of clays in the removal of dyes like cationic, anionic and azo dyes and clays exhibited different adsorption capacities varying from as low as 7 mg/g to as high as about 200 mg/g. Some of the dye removed by various types of clays include: Acid Orange 7 dye by clay and red mud mixes (Hajjaji et al., 2016); Brilliant green dye by red clay (Rehman et al., 2013); methylene blue and methyl orange by bentonite (Fosso-Kankeu et al., 2014); Congo red by a mixture of Kaolin and Bentonite clay (Vimonses et al., 2009) and Reactive red 120 by raw clay (Errais et al., 2012). Table 3 shows various adsorption capacities obtained by different clays for the treatment of various dyes.

5.2. The relationship between clay surface area, size/mesh and adsorption capacity

The major reason for the high adsorption capacity of clay materials is their high surface areas. If a particular clay has a higher surface area, it means that it will also have a higher adsorption capacity compared to clays with lower surface areas (Cadena et al., 1990). However, this notion may not always be the case for some clays but a number of studies have proved that the surface area of a clay is directly proportional to the adsorption capacity of the clay (Sarma et al., 2016; Santos and Boaventura, 2016; Elmoubarki et al., 2015; Auta and Hameed, 2013).

Elass et al. (2011) investigated the removal of methyl violet from aqueous solution using Moroccan clays. Their study showed that the fine mineral fraction had a surface area of 137 m^2/g. As it is expected of high surface area clays, the Morrocan clays had an adsorption capacity of 625 mg/g. The adsorption capacities of other clay based adsorbents for dyes obtained by some other investigators are presented in Table 3. Comparing of these values with the one obtained by Elass et al. (2011) shows that the stevensite-rich clay from Morocco has a comparable higher surface area and high adsorption capacity too. The authors however made an overall conclusion that the mechanisms of adsorption could be explained by electrostatic attraction between the surfaces of the clay which are negatively charged and the dye molecules which are positively charged and not highly dependent on the high surface area of the clay. However, as the clays have a notable higher surface area, the fact that the higher surface area contributed to the high adsorption capacity cannot be ruled out.

On a different study by Yan et al. (2015), the notion that if a particular clay has a higher surface area, means that it will also have a higher adsorption capacity does not hold true. Their study focused on using cetyltrimethyl ammonium bromide (CTMAB) modified organobentonite to remove acid dyes from aqueous solution. The BET results showed that the specific surface area of the modified clay which was measured to be 4.42 m^2/g is comparable lower than that of other adsorbents (Table 3) and even lower than that of raw bentonite (10.2 m^2/g). According to Yan et al. (2015), the reduction in surface area indicates the entrance of organic molecules into bentonite interlayers leading to the blockage of layer channels and thus reducing the surface area. A similar phenomenon was reported by Heinz et al. (2007). Even though CTMAB-Bent recorded a very low surface area it showed very interestingly high adsorption capacities for different dyes. From the Langmuir isotherm results, the maximum adsorption capacities of CTMAB-Bent for Acid Blue 25, Acid Blue 93 Acid Turquoise Blue A, Acid Turquoise Blue A and Acid Golden Yellow G are 360.8 mg/g, 226.0 mg/g, 487.2 mg/g and 304.7 mg/g, respectively. For a clay with a surface area of below 5 m^2/g, the reported adsorption capacities are obviously very high and therefore it can be established that other characteristics of the soil other than its surface area played a vital role in the adsorption of the four dyes.

The surface area of an adsorbent including its pore size are largely important in the description of adsorbent quality because they directly affect their analyte retention abilities and for that reason it becomes imperative to choose adsorbents with high surface area before conducting studies. In a bid to increase the

Table 3
Adsorption capacities of different clays.

Type of clay	Dye removed	Adsorption capacity (mg/g)	Reference
Sepiolite clay	Direct Blue	106	Santos and Boaventura, 2016
Palygorskite	Methylene blue	132.72	Mu and Wang, 2016
Red mud	Acid Orange 7	32.36	Hajjaji et al., 2016
Acid Activated Kaolinite	Congo Red	12.36	Hai et al., 2015
Bis-imidazolium modified bentonite	Telon dyes	108	Makhoukhi et al., 2015
Montmorillonite	Methylene blue	74	Zhou et al., 2014
Acid modified clay beads	Methylene blue	223.19	Auta and Hameed, 2012
Safi decanted clays	Malachite green	88.70	Elmoubarki et al., 2015
Modified natural bentonite	Di azo dye	7.14	Toor and Jin, 2012
Modified montmorillonite	Methyl Orange	24	Chen et al., 2011

surface areas of clays, researchers tend to chemically modify their adsorbents to increase their surface areas (Hai et al., 2015). Auta and Hameed (2012) reported on the effects of modifying surface areas of Raw Ball Clay (RBC) by H_2SO_4. The RBC and Modified Ball Clay (MBC) BET surface area, pore width and total pore volume were found to be 10 m^2/g, 19.62 nm, 0.0519 cm^3/g and 92 m^2/g, 9.54 nm, 0.2183 cm^3/g, respectively. The surface area and pore volume of MBC, were expectedly higher than those of RBC. A possible explanation to this is the leaching and loss of some ions during the acid treatment and calcinations processes. Watanabe et al. (2011) reported similar results after ultrasonically treating SP (0.0)-cal which led to an increase in both surface area and sphere pore volume. Auta and Hameed (2012) reported an 82% increase in surface area which then led to a 188.60% in adsorption capacity with MBC. Results of all these studies show that indeed some chemical treatments to raw clay can increase surface areas and ultimately leading to increased adsorption capacities of modified clays.

The vital part played by surface area on adsorption processes has been shown by various studies on the adsorption of dyes by different clays including kaolinite, montmorillonite and smectites. Table 3 shows numerous clays used for dye adsorption, their surface areas and their adsorption capacities. From Table 4 we can derive a clear relationship between surface areas and adsorption capacities.

The size of clay particles plays an indispensable role in all interphase interactions in clays including ion-exchange and adsorption processes (Mandzhieva et al., 2014). Therefore, the evaluation of the effect of the particle size on the adsorption properties of soils is a vital mission in adsorption processes. Small particle sizes causes equilibrium to be achieved more easily and near maximum adsorption capability can be attained because they reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent.

To examine the effect of the particle size on basic green 4 adsorption by granular organo–inorgano pillared clays (GOICs) in column reactor, Cheknane et al. (2016), varied particle size ranges of GOICs from 300–400 μm to100–1200 μm. Results show that a decrease in particle size improves the performance of the adsorption column from 221 to 428 mg/g. According to their previous work, the adsorption capacities of dye depended strongly on granulation and particle size of the granule pillared clay (Cheknane et al., 2010; 2012). On the other hand, the comparison between the adsorption capacities of BG4 (mg/g) determined from respective batch and continuous reactors, showed the same decrease of adsorption capacity with the size of particles.

The authors explained the observed behavior using the following mechanism:

Firstly, the limitation of active mass of pillared clay to the external surface of granular organo–inorgano pillared clay was influenced by the silicone used for granulating the powder organo–inorgano pillared clay (Cheknane et al., 2010; 2012). Secondly, the interparticle porosity of the adsorption beds are reduced for the small particle size ranges. The column packed with larger particle sized GOICs had lower adsorption efficiencies lower than the one packed with smaller diameter GOICs.

Jaafar (2006) also stipulates that small particle sizes of the clay adsorbent enhance the adsorption capacity of the adsorbent. A study using diatomite for the removal of SB showed that the decreasing of particle size of diatomite from 300 to 60 μm increased the adsorption rate of SB. This is because increasing the external surface area of the diatomite particle exposes more active sites to SB molecules. There is a slight effect of particle size of diatomite on adsorption of textile dyes (Özcan and Özcan, 2004).

5.3. The role of clay morphology in the adsorption process

It is well known that the adsorption capacity of clays depend on

Table 4
Surface area of different clays used in the adsorption of dye.

Clay type	Dye adsorbed	Surface area (m^2/g)	Adsorption capacity (mg/g)	Reference
Red mud	Acid Orange 7	74	32.36	Hajjaji et al., 2016
Sepiolite clay	Direct Blue	108	332	Santos and Boaventura, 2016
Safi raw clays	Malachite green	34.07	156.43	Elmoubarki et al., 2015
Halloysite	Direct orange 34	20	7.75	Chaari et al., 2015
Montmorillonite K10	Crystal violet	173	370.37	Sarma et al., 2016
Acid-activated kaolinite	Azo dyes	358.6	12.36	Hai et al., 2015
Raw clay beads	Methylene blue	58.02	19.32	Auta and Hameed 2013
Modified clay beads	Methylene blue	223.19	101	Auta and Hameed 2013
Raw bentonite	Acid dyes	10.2	–	Yan et al., 2015
CTMAB-Bentonite	Acid Turquoise Blue A	4.42	487.2	Yan et al., 2015
Raw bentonite	Diazo dye	25.7	–	Toor and Jin (2012)
Acid bentonite	Diazo dye	84.6	69.44	Toor and Jin (2012)
Swelling clays	Methylene blue	65	–	Li et al., 2011

their chemical composition and structure (Mu and Wang, 2016). The structure of clay includes crystalline unit growth mechanics, crystallites interlocking and interpenetration, crystal habits including helical growth, twinning, and tapotaxis (Bohor and Randall, 1970). The Scanning Electron Microscope (SEM) is uniquely suited for studying the structure of clays because it magnifies the three dimensional view of clay surfaces with great depth of focus. It brings out the configuration, texture and fabric of clay samples. Fig. 4(a)–(F) shows how SEM can solve the problem of determining the morphology of clay powders. Figures (a) and (b) show Suzhou kaolin with a typical sheet structure and a Longyan kaolin containing tubular Halloysite particles respectively (Zhang et al., 2016). Figures (c) and (d) show natural and Al/Fe oxide-modified diatomaceous earth (DE) respectively and differences pores sizes and DE appearance before and after modification can be seen. The modified DE pores appear to be packed by the deposition of Al/Fe oxide as compared to the clear, net-like pores in the natural DE. The proximate closure of the pores of the modified DE is evidence that natural DE was modified (Izuagie et al., 2016). Figure (e) shows a highly magnified view of a bentonite clay sample and the platy-like features characteristic of clay minerals are seen. Protruding rodlike structures are clearly visible in the montmorillonite rich bentonite clay (Masindi et al., 2015). Figure (f) shows a natural soil sample of smectite rich soils from Limpopo, South Africa. At lower magnifications, the smectite rich clay soils showed irregular porous structure that is a good characteristic of a good adsorbent material (Mudzielwana et al., 2016).

Mu and Wang, 2016 postulates that the effect of different clay origins (which lead to different morphological structures) on adsorption properties of clays is rarely studied. Hence the researchers selected three representative samples of palygorskite (PAL) from Gansu, Anhui and Jiangsu provinces of China to study the effect of different origins on MB adsorption (Zhang et al., 2016). The results revealed that the Mg-poor sample of Jiangsu characterised by short rods and a dioctahedral structure exhibited the highest adsorption capacity for MB, whereas the Mg-rich sample from Anhui characterised by long rods and an intermediate structure of trioctahedral and dioctahedral phyllosilicates exhibited lesser adsorption capacity for MB. From this study we can clearly see how the structures of the selected PAL samples affected their adsorption capacity, showing that it is not only the chemical composition that affects adsorption capacity but morphology. Clays rich in Mg recorded a low adsorption capacity but clays with lower Mg concentrations had a higher adsorptive removal towards MB. Furthermore, it is worth noting that although the maximum adsorption of natural palygorskite toward dyes far exceeded the

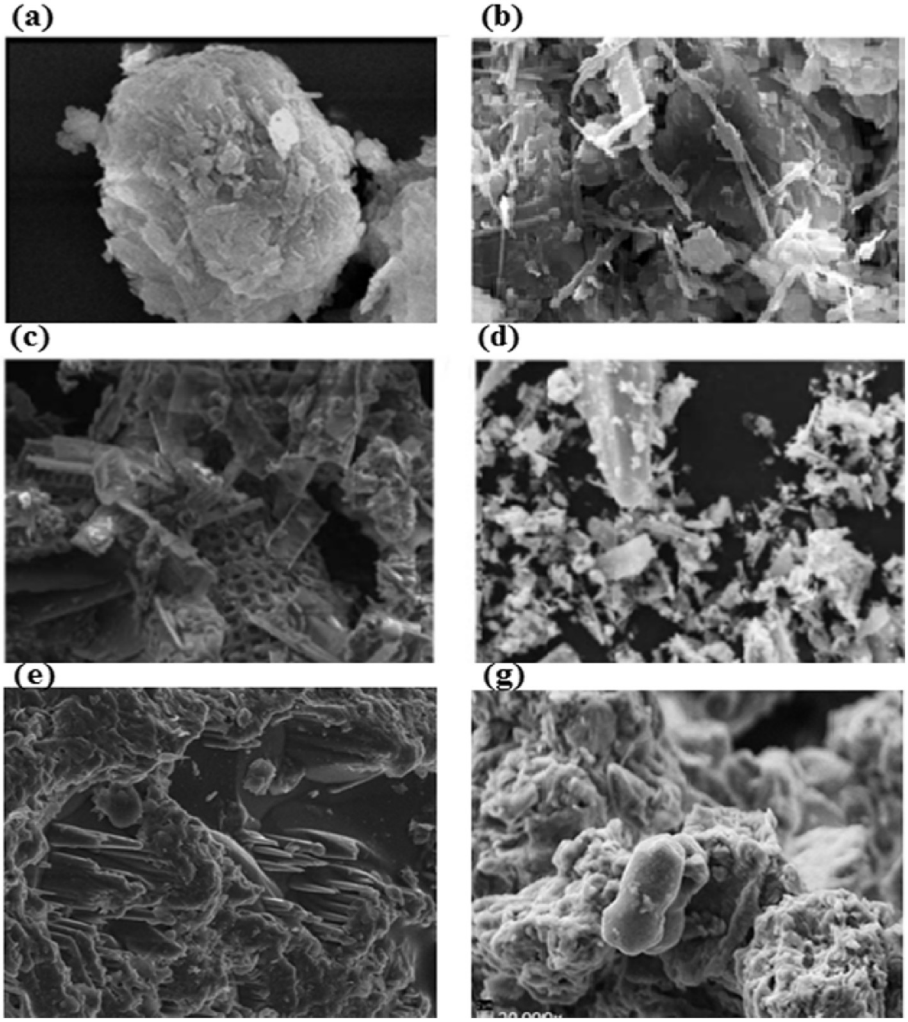


Fig. 4. Clay particles SEM images: (a) - Suzhou kaolin (Zhang et al., 2016); (b) - Longyan kaolin (Zhang et al., 2016); (c) - raw diatomaceous earth (Izuagie et al., 2016); (d) - Al/Fe oxide-modified diatomaceous earth (Izuagie et al., 2016); (e) - bentonite clay (Masindi et al., 2015); (g) - Mukondeni smectite rich clay (Mudzielwana et al., 2016).

cation exchange capacity of palygorskite, it is difficult to completely release the adsorption capacity of palygorskite toward dyes due to the existence of the bulk crystal bundles or aggregates originated from the interparticle Van der Waals' and hydrogen bonding interactions.

Another common structural feature characteristic of clay soils is their fibrous and porous nature. It is interesting to note the difference in adsorption capacities with respect to different dyes on fibrous clays. Sarma et al., 2016 used raw and acid-treated montmorillonite to adsorb CV. With a more similar structure to montmorillonite is bentonite which was studied by Chinoune et al., 2016 for the removal of Procion blue HP (PB) and Remazol brilliant blue R (RB), both anionic reactive dyes. The SEM images of montmorillonite showed that the clay had a fluffy appearance of different shapes and sizes with some bigger particles appearing broken down into small and medium sized particles with no particular shape. On the other hand, bentonite appeared either as thin, ultrafine, leaf-like crystals forming dense aggregates or in a more open honeycomb texture. The Langmuir monolayer adsorption capacities of PB and RB on bentonite in aqueous solution were estimated to be 40.22 and 66.90 mg/g, respectively while the Langmuir monolayer adsorption capacity of raw montmorillonite was found to be 370.37 mg/g. It is very interesting to note how much the adsorption capacities of more or less similar fibrous clays are so different with montmorillonite having an adsorption capacity almost 7 times greater than that of bentonite. The fibrous surface topography of the clays are expected to increase the degree of unsaturation of the surface with dangled bonds and free valences, thus amassing the total surface area of the clay. The lower adsorption capacity of the bentonite clay compared to that of montmorillonite could be due to the dense aggregates in the clays that did not create enough pores to allow for adsorption compared to the broken down particles that appeared on the montmorillonite.

5.4. The role of electrical charges in the adsorption process: point of zero charge (pHpzc), point of zero net proton charge (PZNPC), zeta potential and charge density

Point of zero charge (pHpzc) is among the significant factors which can help indicate the type of surface active centres on the adsorbent and the adsorption ability of the surface (Yagub et al., 2014). The point of zero charge (pzc) is the pH at which the net surface charge is zero and is typically used to define the electrokinetic characteristics of a surface. The value of pH is used to describe pzc only for systems in which H^+/OH^- are the potential determining ions. Studies on point of zero charge (pHpzc) of a number of clay adsorbents have been conducted in order to understand the adsorption mechanism in relation to pzc (Ghaedi et al., 2011; Shirsath et al., 2013; Tümsek and Avci, 2013). Cationic dye adsorption is high at pH > pHpzc because of the presence of functional groups like OH^- while, anionic dye adsorption is high at pH < pHpzc when the surface is positively charged.

Chemical characterization of red clay by Rehman et al. (2013) showed that it had a point of zero charge at pH 6.8. It is well known that dye adsorption is dependent on pH of the solution because the surface charge of the adsorbent and the degree of ionization of the adsorbate and degree of dissociation of functional groups differ with various pHs (Nandi et al., 2009; Ghaedi et al., 2011). The adsorption of Brilliant Green dye by red clay was higher at circumneutral pH. However, the highest adsorption efficiency (97%) and capacity (121 mg/g) was recorded at pH 7. The information on pHpzc of red clay best explains the impact that solution pH has on the adsorption of BG. As stated earlier, the pzc of red clay was established to be 6.8 and the results show BG adsorption is favoured at pH 7. Electrostatic forces operate because the RC surface will be negatively charged at pH > pHZPC, and BG molecules are positively charged. At high pH there is charge neutralization on RC surfaces leading to enhanced adsorption of BG (Ghaedi et al., 2011). At pH > 7 there was no significant adsorption. Nandi et al. (2009) and Shirsath et al. (2013) also studied the adsorption of BG by kaolin clay at pH 7 and they described the same results. However, high BG adsorption capacity (108.4 mg/g) at pH ≤ 4 exposed that BG dye adsorption was not the only due to electrostatic attraction.

Besides the point of zero charge there is also the pH at which there is a zero net adsorption of H^+/OH^-, designated as points of zero net proton charge (PZNPC) (Avena and De Pauli, 1998). A study using sepiolite clay on the adsorption of cationic and anionic azo dyes by Santos and Boaventura (2016) determined the PZNPC at three different ionic strengths by the pH-drift method (Lazarević et al., 2007). The results showed three distinct intersection points for different ionic concentrations: 10.4; 10.0 and 9.8, respectively for NaCl 0.001 M, 0.01 M and 0.1 M. The authors concluded that this observation was due to the dual nature of surface charge in minerals. Where two different surface charges are present: a permanent negative charge (resulting from the structural isomorphous substitutions) and a pH-dependent charge (primarily related to the dissociation of hydroxyl groups). The authors further on reported that the intersection points obtained, corresponding to zero net adsorption of $H+/OH^-$ should be named as PZNPC, instead of PZC, since they represent the conditions where the pH-dependent charge is null (Avena and De Pauli, 1998) and not the conditions under which the total charge is null. The high PZNPC values allowed for the prediction of a higher tendency of sepiolite to adsorb the anionic dye in pH conditions up to 10. The different pH effects observed by Santos and Boaventura (2016) for cationic and anionic species (Han et al., 2014; Tumsek et al., 2013; Tabak et al., 2009) and are explained by the electrostatic attraction. With the increase in pH, the dependent charge tends to be more negative and hence amenable to adsorb cationic species and less to adsorb anionic ones. The PZNPC of sepiolite occurs at pH 10 and then a significant increase in BR dye adsorption was observed from an equilibrium pH 8.5–8.7 to 9.2–9.5; in turn, a sharp decrease in the DB uptake was observed from final pH 9.3 to 9.8.

Greenwood and Kendall (1999) defines zeta potential as "the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface". Zeta potential is an important parameter because its value helps to determine colloidal dispersion stability. It indicates the degree of repulsion between particles with similar charges in a dispersion. So, colloids with high negative or positive zeta potential values are said to be electrically stabilized whereas those with low zeta potential values have a tendency to flocculate (Hanaor et al., 2012). The zeta potential of clays also plays a very important role in dye adsorption and this can be seen when the effect of pH on dye adsorption is investigated (Fayazi et al., 2015).

Zeta potentials of modified sepiolite (MS) and natural sepiolite (NS) at various pHs were determined and it was established that NS and MS isoelectric points were around 6.8 and 7.9, respectively. Comparable values, between pH 3.2 and 7.4 have also been reported by other researchers (Lazarević et al., 2007; Sabah et al., 2007) for the isoelectric point of natural Sepiolite, and 7.7 to 8.5 for that of iron-coated Sep (Liu et al., 2014; Lazarević et al., 2010). The sepiolite used in the various studies had different mineralogical composition and clay mineral preparation methods for electro kinetic measurements differ hence we see a wide range of values for Sepiolite. (Fayazi et al., 2015). The surface charges of adsorbent materials are usually influenced by pH because of the effect it has on the degree of ionization of the adsorbate. When pH is less than 7.9, the MS nanocomposite surface is positively charged because of surface functional groups protonation and when pH is greater than 7.9 the surface is negatively charged due to the dehydroxylation of the MS surface groups. In acidic conditions, the H^+ compete with positively charged dye molecules for available adsorption sites, hence the decrease in removal efficiency. As pH increases, there is also a rise in removal efficiency due electrostatic attraction between the negatively charged surface of the MS nanocomposites and cationic Safranin molecules. Given the above, we can then say pH has a very important role to play in adsorption processes.

5.5. Clay charge density and swelling properties: effect on the adsorption process

The reactivity of clay minerals is commonly due to a charge they carry. The presence of this charge is the basis of their exchange capacity and consequently swelling. The relationship between clay charge and swelling lies in the fact that as clay charge density increases, the attraction energies on the clay predominate and therefore the clay does not swell, whereas the vice versa is true with decrease in charge density (Miyamoto et al., 2000). There are three main groups of clay minerals which are kaolinite, illite and smectites (Liu and Zhang, 2007). Nevertheless, the most commonly used clays in dye adsorption processes are smectites and kaolinites. Structurally, illite clays are similar to muscovite, but are typically deficient in alkalis, with less Al substitution for Si and because of possible charge imbalance, Ca and Mg can also sometimes substitute for K. The K, Ca, or Mg interlayer cations prevent the entrance of H_2O into the structure hence making this type of clay to be non-expanding clays (Moore and Reynolds, 1997). Just like illite clays, kaolinite also does not absorb water and does not expand when it comes in contact with water. However, smectites or montmorillonites show a different behavior when contacted with water. Smectites are weakly linked by cations like Na^+, Ca^{2+} which result in the high swelling/shrinking potential of this type of clay. The interlayer in smectites is not only hydrated, but it is also expansible and because of this, they are often referred to as “swelling clays” (Grim, 1962).

The charge densities of clay minerals are important not only for structural studies but in the application of clays in the adsorption processes. Whether or not a clay becomes totally dissociated or not, depends on the available interlayer cations and the layer charge (Liu and Zhang, 2007). For example, vermiculites have a high charge and for that reason, they will not completely dissociate. Essentially, without a charge, kaolinites are never separated to start with, because they do not have interlayer cations that hydrate. However, they can undergo interparticle swelling as opposed to intraparticle swelling. Unlike the other two types of clays, smectites will undergo complete dissociation by osmotic swelling when saturated with cations possessing a hydration energy greater than or equal to Na^+ (Moore and Reynolds, 1997).

Numerous clay adsorption properties can be associated with the layer charge density (Mermut, 1994). Bujdák and Komadel (1997) studied the interaction between modified clays with different layer charges and the cationic dye (methylene blue) in aqueous suspension. The authors concluded that the strong aggregation and redistribution of the molecules in the clays with higher layer charge was due to the proximity of the negative sites in the clay surfaces and the different coverage of the clay surfaces. This suggests that MB is initially adsorbed only on a minor fraction of the clay, followed by a redistribution with passing time. The higher layer charges on the particles of the studied montmorillonites resulted in a larger aggregation of the dye. The higher charge holds together the layers of the clay more tightly, preventing the movement of the dye molecules to the interlamellar region. The effect of layer charge density in the adsorption of dyes by numerous layered silicates was also examined by other authors (Miyamoto et al., 2000; Bujdák et al., 2010).

Bentonite possesses an excess negative charge on its lattice and is characterized by a three-layer structure having two silicate layers covering an aluminate layer (Adeyemo et al., 2015). This comes as a result of the partial replacement of tetravalent Si with trivalent Al that leads to the replacement of trivalent Al with divalent Ca. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye. Therefore, it can be expected that bentonite clay exhibits a greater capacity to take up cationic dyes. On the other hand, kaolinite has a heterogeneous surface charge. The basal surface of kaolinites is believed to carry a constant structural charge, which is attributed to the isomorphous substitution of Si^{4+} by Al^{3+}. The presence of a charge on the edges is a result of protonation/deprotonation of surface hydroxyl groups and therefore depends on the solution pH (Zhou and Gunter, 1992). Kaolinite is reported to be the least reactive clay (Suraj et al., 1998). However, it's high dependency on pH increases or constrains the adsorption of dyes according to the pH of the solution (Mitchell, 1993). Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets (Spark et al., 1995).

Extensive studies have been done utilization swelling clays to eliminate cationic dyes from aqueous media. Many of these studies sought to evaluate the applicability and feasibility of using basic dyes adsorption for cation exchange capacity (CEC) and specific surface area (SSA) determination. Li et al. (2011) did a study to explain the mechanism of MB adsorption on low-charge montmorillonite as a swelling clay. The stoichiometric desorption of exchangeable cations from the clays associated with MB adsorption together with the close match between the CEC of the clays and adsorption capacity established cation exchange as the central mechanism for MB elimination. XRD and TG—DTG analyses indicated interlayer adsorption, hence, intercalation of MB molecules. FTIR analyses indicated that hydrogen bonding might not be a major interaction in the adsorption of MB. The results confirmed that the charge density, rather than the SSA was the limiting factor for MB adsorption. The authors concluded that for the treatment of wastewater having cationic dyes, swelling clays with a high CEC values would be efficient adsorbents.

Another study by Lv et al. (2011) also confirmed that with low charge swelling clays, CEC is the single most important mechanism for dye removal from water. Lv and coworkers investigated the adsorption of acridine orange (AO), a cationic dye, on low charge montmorillonite to better understand the mechanism behind AO removal using swelling clays. The proportional desorption of exchangeable cations from the clays followed by AO adsorption established cation exchange as the most leading mechanism for AO removal. Moreover, FTIR analyses confirmed the presence of cationic dye AOH^+ on the surface and in the interlayer of the swelling clays. XRD and TG-DTG results also showed interlayer adsorption, thus, intercalation of AO molecules with different conformations at low and higher AO adsorption levels. The authors then concluded that the amount of AO adsorbed far exceeded the CEC of the low charge swelling clays and that was seen as an advantage of using swelling clays to remove cationic dyes from water. They further reported that the uptake of AO was attributed to cation exchange when the amount of AO adsorbed was less than the CEC.

6. Disadvantages of clays leading to modification to enhance their adsorption capacities

Although clays have shown to be good adsorbents for dyes, they have several limitations which have led to several forms of modifications to enhance their adsorption capacities. Clay modification is the introduction of an alien material to clay matrices with the aim of improving its adsorption capacity for a given pollutant. There are different ways of clay modification which include pillaring, mechanochemical modification, ion exchange, organo-modification and sonochemical treatment. A variety of studies have reported on the modifications of clay including chemical treatments such as $Mg(OH)_2$ coating of bentonite (Chinoune et al., 2016), clay ion-exchange using bis-imidazolium salts (Makhoukhi et al., 2015), quaternary ammonium cationic surfactants addition onto bentonite external surfaces (Yan et al., 2015), modifying bentonite by a cationic surfactant (Hexadecyltrimenthylammonium chloride) (Anirudhan and Ramachandran, 2015) and treating the clays with acid (Espantaleon et al., 2003; Özcan and Özcan, 2004).

6.1. Cationic and anionic surfactant modification

Generally, clays are applied in the elimination of basic dyes because they have a natural negative charge but chemical modifications to the surfaces of the clay can change the surface charge of clays from negative to positive (Errais et al., 2012). These alterations enhance the sorption of anionic dyes. Baskaralingam et al. (2006) stipulates that bentonite adsorbs acidic pollutants weakly because of repellant forces between the negatively charged surfaces and the anions. A number of authors have reported on the modification of bentonite with cationic surfactants for the removal of acidic dyes. They showed that the main mechanism of the acidic dye adsorption can be can be explained in terms of the anionic exchange between the excessive anions and the cations from the surfactant (Ceyhan and Baybas, 2001; Jovic-Jovicic et al., 2008; Ozcan et al., 2004). Ma et al. (2013) compared the performances of raw bentonite and surfactant-modified bentonite. Their findings showed that CTAB-modified bentonite has a comparable high adsorption capacity towards acid dyes, whereas the raw bentonite showed a lower adsorption capacity. The adsorbed amount of Cong Red was found to be 210.10 mg/g for CTABMBn and 37.10 mg/g for raw bentonite.

Clays are also known to have low organic carbon content and because of their hydrophilic surfaces, they are usually less effective in adsorbing nonionic organic contaminants in water (Boyd et al., 1998). However, simple ion-exchange reactions with surfactants causes the clay to be altered from being organophilic to being organophobic and hence enhancing nonionic organic contaminants adsorption. Studies have shown that cationic surfactants intercalation does not only change the hydrophilic surface characteristics of the clay, but it also significantly increases the clay interlayer basal spacing. Many studies have investigated the modification of montmorillonite (MMT) by alkyl quaternary ammonium cationic surfactants like dodecyltrimethylammonium, benzyldimethylteradecylammonium and cetyltrimethylammonium. Few studies have reported on anionic surfactant modification mainly because anionic surfactants have a negative charge thus making it difficult to enter into the interlayer spacing of the clays (Zhang et al., 2011).

Chen et al. (2011a) disclosed that surfactants that are anionic enter the interlayer space as pairs of ions with protons (H_3O^+ ions) or as counter ions (Na^+ and Ca^{2+}). Zhu and Chen (2000) studied the adsorption characteristics of MMT modified by an anion–cationic surfactant and they established that a combination of cationic and anionic surfactants form mixed micelles, producing organic compounds synergies solubilization. On another study Chen et al. (2011), modified MMT by anion–cationic, anionic and cationic surfactants by adding anionic surfactants cetyl trimethyl ammonium bromide (CTMAB) and anionic surfactants sodium stearate (SSTA) to MMT. The mechanisms of adsorption of methyl orange on anion–cationic modified MMT were compared. Their findings showed that CTMAB/10SSTA–MMT has a higher adsorption capacity than CTMAB–MMT and 10SSTA–MMT because of the formation of a highly effective partition medium by anion–cationic surfactant micelle.

Li et al. (2010) reported on the adsorption of a polymer loaded bentonite (EPIDMA) and raw bentonite for Acid Scarlet (AS GR) and Acid Dark Blue 2G (ADB 2G) dyes from aqueous solution. After the adsorption experiments, the adsorption capacities of raw bentonite, cationic surfactant cetyltrimethylammonium bromide (CTMAB) modified bentonite (CTMAB/bentonite) and cationic polymerpolydiallydimethylammonium (PDMDAAC) modified bentonite (PDMDAAC/bentonite) were compared. For AS GR, the observed adsorption capacities were 4.12, 30.28 and 42.72 mg/g for raw bentonite, CTMAB/bentonite and PDMDAAC/bentonite respectively whereas for ADB 2G the adsorption capacities were 3.67, 24.85 and 33.34, respectively for the three different adsorbents. All the above mentioned adsorption capacities were lower than that of EPI-DMA/bentonite for AS GR and ADB 2G which recorded maximum adsorption capacities of 45.54 and 35.93 mg/g respectively. This comparison study confirmed that EPI- DMA/bentonite is the best adsorbent for AS GR and ADB 2G among the selected adsorbents.

6.2. Magnetic modification

Due to their high dispersion, waste clay particles can prove difficult to remove from solution after adsorption. To overcome this limitation, magnetizing clays can be an option using a simple procedure referred to as magnetic separation which removes the clay particles from water (Xu et al., 2012; Gao et al., 2015; Wang et al., 2014). Magnetic materials such as ferrite (MFe_2O4, where M = Co, Mn, Cu, Zn, etc), Fe_3O_4, Fe_2O_3 and so on have been used as adsorbents for the removal of toxic pollutants because they can be easily separated from the reaction medium by using an external magnetic field within a short time. Unfortunately, their low adsorption capacity and narrow pH range restrict their large-scale practical application (Li et al., 2016). Therefore, to improve adsorption performances, great efforts have been made to functionalize magnetic materials (Fan et al., 2012; Ge et al., 2012; Peng et al., 2012).

The introduction of magnetic particles in the nano scale industries is attracting the attention of numerous researchers (Hashem, 2013). Nano particles are exceptionally fine sized and this property makes them favorable adsorbents. When the size of a particle is reduced, the surface of the particles becomes more accessible to atoms resulting in an increased surface area ultimately changing the surface morphologies and surface energies of the nanoparticles. The aforementioned factors modify the elementary properties and the chemical reactivity of nanomaterials (Hashemian, 2010). Hashem (2013) studied the effect of covering bentonite nanocomposite with magnetite on the removal of methylene blue. According to the author, the introduction of Fe_3O_4 magnetic nanoparticles into the surface of bentonite generates a porous surface with high surface area which is suitable for the adsorption of cationic dyes such as methylene blue. The findings of the batch adsorption experiments revealed that, increasing the initial pH of MB solutions as well as the contact time also increased the adsorption capacity. However, a different trend was observed with adsorbent dosage as the adsorption capacity decreased with increasing mass of the adsorbent. The maximum adsorption capacity was 1600 mg/g.

Another reason why magnetic materials are preferred in the adsorption process is because they have been proved to have more advanced mesoporosity and microporosity compared to natural clays (Giakisikli and Anthemidis, 2013). Ambasht and Sillanpa (2010) also stipulated that magnetic composites have high surface areas compared to natural clay and this makes them to produce fast adsorption kinetics i.e. comparatively little contact time is needed for the adsorption process to reach equilibrium. Determination of sorption properties of magnetic nanocomposite sorbents showed that the adsorption efficiency of nanocomposites is considerably greater than the separate phases of the composite. Moreover, studies have shown that all the residual composite magnetic sorbents can be successfully removed from aqueous solution by magnetic separation (Makarchuk et al., 2016). A study to assess the adsorption of MB by nanocomposite sorbents, saponite and magnetic liquid revealed that among the three tested adsorbents, the magnetic composite sorbents (MCS) were the most effective adsorbents. With respect to all dyes, the adsorption capacity of MCS increased as the magnetite content increased from 2 to 7 wt%. However, modifying saponite by magnetite by 10 wt% led to the decrease of MCS 10 sorption properties. These results corroborated with the characteristic of nanocomposites porous structure.

6.3. *Mechanochemical modification of palygorskite*

Mu and Wang (2016) compiled a comprehensive review on the modification of palygorskite with different physical or chemical methods and palygorskite-based composite used as adsorbents for the adsorption of dyes from aqueous solution. Traditionally grinding and extrusion methods were widely used on palygorskite to modify it to increase its adsorption capacity before use because of their simple operation process, low cost, and easy industrial application. However, the enhancement in the adsorption capacity of palygorsite toward dyes is limited by these traditional methods. Therefore, other treatments also have been adopted to activate palygorsite for the adsorption of dyes, such as acid- or alkali-activation, thermal treatment, hydrothermal or solvothermal treatment. To have a full understanding on the various mechanisms involved in the dye removals and specifications in the modification processes, readers are advised to consult the review article by Mu and Wang (2016). However Table 5 summarises some of the methods of palygorsite modifications that have been used and how these various modifications impacted the adsorption capability of the palygorsite. Because palygorsite is an example of a clay, the same modifications can be applied to some clays.

6.4. *Structural and chemical changes after clay modification: effect on adsorption*

To follow the structural and chemical changes made after various modifications, the adsorbents are usually characterised before and after modifications. Most modifications are aimed at increasing the surface area of the clay soils or adding the functional groups that are responsible for dye uptake and all this will be basically aimed at enhancing the adsorbent material's adsorption capacity. Sarma et al., 2016 reported on the treatment of montmorillonite (Mt) with 0.25 and 0.50 M sulfuric acid and how this treatment affected the adsorption capacity of the clay. Characterization by BET showed that pore volume and surface area were greater than before acid treatment. The pore volume showed an increase from 0.1 cm^3/g to 0.8 cm^3/g after treatment and the surface area increased from 173.0 to 221.38 m^2/g and further to 228.95 m^2/g on treatment with 0.25 M acid and 0.50 M acid respectively recording a 28 and 32.3% increase for the different acid molar concentrations respectively. This increase in surface area may have led to the increase in adsorption capacities as reported by the authors. The Langmuir data disclosed that the adsorption capacity of the untreated montmorillonite was 370.37 mg/g while that of 0.25 M and 0.50 M acid treated montmorillonite was 384.62 and 400.0 mg/g respectively at 303 K. Treatment with acid removes impurities in the clay at the same time substituting exchangeable cations with H^+. Acid treatment can also lead to cation leaching some from the tetrahedral and octahedral sites opening up platelet edges. This may result in an increase in the surface area and the pore dimensions (Diaz and Santos, 2010; Auta and Hameed, 2013) subsequently leading to an enhanced adsorption capacity.

Anirudhan and Ramachandran (2015) used Hexadecyltrimenthylammonium chloride as a cationic surfactant to modify bentonite clay. Characterization of the clay before and after modification showed significant changes in the chemical composition and surface properties of adsorbent. The changes included a decrease in Fe_2O_3 and Al_2O_3 content, implying that the surfactant adsorption was through the exchange of inorganic cations, the BET surface area of the organoclay was reduced from 36.5 to 27.9 m^2/g. Unlike surface area, the PZC and CEC of the bentonite increased after modification from 4.5–7.8 and 0.52–0.71(meq/g) respectively. The prepared organo bentonite clay was later evaluated for its adsorption behaviour for the basic dye removal CV, MB and Rhodiamine B (RB). The findings showed that the modified clay demonstrated better adsorption capacity for the removal of all the selected dyes. pH was found to play an imperative role in the adsorption process, moreover the removal of dyes was found to be dependent on initial dye concentration. The adsorption capacities for the dyes were established to be 399.74 mol/g for MB, 365.11 mol/g for CV and 324.36 mol/g for RB. The adsorption efficiency of the organobentonite was higher than the unmodified bentonite as expected. The results also showed that organoclay was 1.6, 1.7 and 1.75 times more effective than natural bentonite for MB, CV and RB adsorption respectively because after modification, the porosity of the clay increased. The authors attributed the mechanism of the adsorption process to the adsorption/partition model (Zhu and Chen, 2000). This study basically showed us that surfactant modification of clay can enhance their adsorption capacities.

In a study done by Chinoune et al. (2016), an effective brucite-coated bentonite was synthesised and assessed for anionic dye removal from water. The obtained results from this study showed that, coating bentonite clay with $Mg(OH)_2$ considerably improved the removal of reactive dyes. At a pH of 5, which was greater than the acidity constant, reactive dyes mainly existed as anions and were probable going to be repelled by the montmorillonite surfaces because they are negatively charged. The B–$Mg(OH)_2$ contains more polar acid Si–O– groups and basic Mg(OH) sites that have a tendency to react with organic compounds because they are polar in addition to several other functional groups. The ability of modified bentonite to take up dyes showed that van der Waals and $\pi-\pi$ interactions take place amongst OH ions available on the clay. pH had a major influence on the adsorption of ions on the composite surface, mainly on the extent of adsorbate ionization. The maximum dye removal was achieved at pH 2. This could be as a result of electrostatic interaction between cationic dye molecules and the negatively charged B–$Mg(OH)_2$ surfaces. Nonetheless, the adsorption still took place in basic conditions, showing the occurrence of intermolecular interaction.

On the work done on bentonite, Ozcan et al. (2004) proposed that natural bentonite surfaces makes it less effective for taking up hydrophobic organic compounds owing to the electrical charges and hydrophilic surface. The authors recommended that raw bentonite can be treated by organic cations to yield a Dodecyltrimethylammonium bromide-modified bentonite (DTMA-bentonite) thus considerably improving its ability of adsorbing hydrophobic pollutants from aqueous solution. A comparison of the findings with Na-bentonite revealed that Na-bentonite and DTMA-

Table 5
Various palygorsite modifications for the adsorption of dyes.

Modification method	Dye removed	Effect of modification on adsorption capacity	Reason for change in adsorption capacity	References
Extrusion	Methylene blue	Adsorption capacity was observed to increase to 158 mg/g, 78 mg/g and 98 mg/g.	Partial disaggregation of crystal bundles of PAL.	Zhang et al., 2015a,b
Grinding	Methylene blue	Percentage dye removal increased by 25%	Specific surface area increased from 153 to 229 m^2/g.	Liu et al., 2012
High-pressure homogenization	Methylene blue	Percentage dye removal increased by 21%	Disaggregation of PAL crystal bundles.	Zhang et al., 2015a
Ion beam bombardment	Methylene blue	Better adsorption capacity in comparison to the raw PAL.	A larger interspace, better separation, higher pore-size (with micro/nano- scale) and porosity, and doubling of the BET surface area of the PAL nanonetworks.	Cai et al., 2010 Zhang et al., 2013
Acid activation	Quinalizarin	Percentage dye removal increased by 50%	Increase the surface area.	Frini-Srasra and Srasra, 2009
Alkali-activation	Methylene blue	Exhibited a far better adsorption capacity compared to that of raw PAL inferred from the colour of 200 mg/L MB.	No clear explanation because the rod-like morphology almost disappeared and BET specific surface area of PAL was highly reduced after the treatment with 5.0 M of NaOH solution.	Wang et al., 2015
Thermal activation	Methylene blue	Adsorption capacity increased with calcination temperature and reached the maximum at 700 °C (about 78.1 mg/g), and then decreased with further increasing temperature.	Cation exchange was a main mechanism in the adsorption process.	Chen et al., 2011b
Hydrothermal or solvothermal treatment	Methylene blue	Adsorption properties of PAL for MB were evidently improved from 119 mg/g to 171 mg/g after modification	Disaggregation of crystal bundles, PAL nanorods became more uniform and an increase in pore size of adsorbent.	Zhang et al., 2015b
Surfactant modification	Orange II	Adsorption capacities were observed to be 92 and 88 mg/g.	Electrostatic attraction as well as van der Waals interaction.	Sarkar et al., 2011
Silane coupling agent modification	Reactive Red 3BS, Reactive Blue KE-R and Reactive Black GR	34.24 mg/g, 38.60 mg/g, and 60.13 mg/g respectively. Percentage increase from 1.16 to 99.32%; 3.30–99.67% and 2.88–96.42% respectively.	Activity of the amino groups.	Xue et al., 2010 Xue et al., 2011
Polymer modification	Reactive yellow 3RS	Langmuir model was 71.38 mg/g which was much higher than that of the raw PAL (6.3 mg/g).	Cationicity	Peng et al., 2013

bentonite synthesized from natural materials are able to remove acid blue 193 from aqueous solution. Nevertheless, DTMA bentonite displayed a greater removal capacity than raw bentonite. DTMA-bentonite had an adsorption capacity of 740.5 mg/g which is approximately 11 times greater than that of Na-bentonite (67.1 mg/g). Acid blue 193 was also adsorbed effectively by Özcan et al. (2005) by treating bentonite using benzyltrimethylammonium (BTMA) chloride surfactant. Furthermore, Ozcan et al. (2007) applied the DTMA-bentonite for the elimination of reactive blue 19 from water. The results showed that the modified bentonite had an adsorption capacity of 206.58 mg/g for DTMA-bentonite at pH of about 1.5. This suggested that electrostatic interactions occurred between bentonite's adsorption site and the anionic dye.

6.5. *Clay composite materials: clay nanocomposites, clay/polymer nanocomposite and clay/polymer nanocomposite hydrogels*

One promising approach to resolve the disadvantages of the low adsorption capacities of natural clay minerals is to mix it with other advanced adsorbents like polymers and/or activated carbon which have proven to be exceptionally efficient in the removal of organic compounds. In recent years, composite materials have received extensive interest for their potential applications in wastewater treatment because they can combine the properties and advantages of each component and may also exhibit some attractive performances (Mahdavinia et al., 2012a; Hosseinzadeh et al., 2015). A composite could be defined as a mixture of two or more materials possessing different physical and chemical properties with a very distinct interface.

Dye adsorption onto clay minerals is affected by different factors like exchangeable cations, the space between the clay inter layers, and whether or not there are water molecules between those layers. On the other hand, polymers are considered multipurpose materials because they can be easily manipulated, they are simple to produce and are highly flexible. However, there are cases where polymers need to be altered for them to achieve certain performance requirements. One way of modifying polymer properties is mixing them with solid fillers such as fibers, platelets, particles, other polymers, clays or clay minerals, resulting in polymeric composites or blends (Mahdavinia et al., 2012c). These polymeric blends can then be used for adsorption processes and studies have shown that they exhibit exceptionally good adsorption capacities (Table 3).

There are different types of polymers used for adsorption processes and hydrogels are amongst those polymer materials performing successfully in the removal of contaminants from aqueous solution. They are a group of polymers capable of absorbing a lot of water without dissolving because of the physical or chemical crosslinking of the hydrophilic polymer chains (Schacht, 2004). Hydrogels have functional groups that can ionize easily and therefore repel each other, capturing more water molecules. Additionally, these ionized functional groups let hydrogels absorb and trap different types of contaminants with the opposite ionic charges. As such, hydrogels, as potential adsorbents have attracted much attention in recent years for dye adsorption. Furthermore hydrogels have a relatively low production cost and high adsorption capacity for some dyes (Wang et al., 2010).

Kamal et al. (2014) prepared copolymer hydrogels made up of Poly vinyl alcohol (PVA) and Poly acrylic acid (PAA) through γ-irradiation. This polymer was prepared having *N*,*N*′ methylene bis acrylamide (MBAM) as a crosslinking agent. The adsorption experiments revealed that the adsorption of CV dye onto PVA/PAA and PVA/PAA/clay composite hydrogels depended on a number of variables like solution pH, concentration dye concentration, PVA/PAA/clay composition, temperature of the solution and ionic strength amongst other variables. It can be concluded that the PVA/PAA/clay composite hydrogel is a more efficient adsorbent than PVA/PAA hydrogel for CV dye, since its removal efficiency reached 92% for the composite hydrogel containing 4% clay and of composition 50/50 (wt%).

Clays like bentonite, laponite, sepiolite enhance the adsorption capacity and mechanical properties of hydrogels and in most cases nanocomposite hydrogels are loaded with such types of clays (Shirsath et al., 2011). A study that corroborate this findings was carried out by Li et al. (2012) where nanocomposites hydrogels were prepared by loading laponite clay into a poly(acryl amide) hydrogel via in situ polymerization to assess the adsorption properties of the composite onto CV. The experimental results of the removal of cationic dye showed that, as the clay content in the hydrogel increased, the adsorption capacity of the hydrogel increased hence confirming the aforementioned statement about clays enhancing the adsorption capacity and mechanical properties of hydrogels. Li and coworkers also prepared another hydrogel nanocomposite (poly(acrylic acid)-bentonite-FeCo (PAA-B—FeCo)) through ultrasound assisted in situ emulsion polymerization. The incorporation of Fe—Co and exfoliated bentonite clay platelets also increased the stability and strength of hydrogel thereby aiding the dye adsorption process. The adsorption results showed that a pH of 11 produced the maximum dye adsorption because at that high pH, there is dissociation of COO— ions which attracts cationic organic compounds.

Adsorption studies using a variety of composites including nanocomposites, polymer composites, clay nanocomposites hydrogels has acquired relevance due the potential it offers, as shown on Table 6.

7. The effect of variables and their interaction on dye adsorption

Dye adsorption studies using clays are usually carried out in a batch approach to evaluate the influence of experimental parameters including contact time, pH, adsorbent dose, initial dye concentration and temperature. Batch experiments investigate one factor a time in order to acquire optimum conditions of dye adsorption.

7.1. *Effect of solution pH*

By definition, pH is a measure of hydrogen ions concentration. The variability of the pH of the aqueous solution in which the adsorption process takes place, plays a vital role in the whole adsorption process (Elmoubarki et al., 2015). Generally, pH influences the dye adsorption because of change in surface characteristics of the adsorbent and that of the dye chemistry. Solution pH also determines the extent of protonation of the OH^- exchange sites and the extent of protonation of the adsorbate thus determining the specific charge of an exchange site and therefore ultimately the adsorption tendency of the substrate also (Tomar et al., 2014). Therefore the adsorption capacity of the adsorbent will also depend on solution pH. In general, at low pH values (acidic conditions) there is an increase in the amount of anionic dye removal. This is due to the electrostatic attraction occurring between the anionic dye and the positively charged surface of the adsorbent. At high pH values (basic conditions), there is electrostatic repulsion between the negatively charged adsorbent surface and the anionic dye, therefore reducing the adsorption capacity and anionic dyes percentage removal (Han et al., 2014; Tümsek and Avci, 2013).

To corroborate the general trends shown by the effect of pH on dye adsorption, we looked at a few studies that investigated pH influence on the removal of dyes from solution. To study the effect of pH on adsorption, Anirudhan and Ramachandran (2015) performed batch experiments using organoclay on dyes with initial concentrations of 200 and 400 μmol/L solutions of Methylene Blue (MB), Reactive Blue (RB) and Crystal Violet (CV). The findings showed that increasing pH also increases the adsorption capacity. A possible explanation to this observation is that, increase in pH, decreases the positive charges on the surface thereby increasing the negatively charged sites. Negatively charged surfaces on the clay will favour the uptake of cationic dye molecules due to electrostatic attraction. Earlier we mentioned that cationic dye adsorption improves with a rise in pH. Results on the specific adsorption capacities of the of the clay for dyes were 99 and 97 μmol/g for MB, 95 and 184 μmol/g at initial concentrations of 200 and 400 μmol/L for CV and 90 and 174 μmol/g for RB, respectively at pH 9. The dyes were taken up in the order: MB > CV > RB. The authors reported that order of affinity could be explained on the basis that dyes have different molecular size, structure and functional groups hence electrostatic and other physical forces they experience will be different (Allen et al., 1989). Essentially most cationic dyes yield molecular cations (C^+) as well as reduced ions (CH^+) (Kavitha and Namasivayam, 2007). There is a decrease in dye adsorption in acidic conditions due to the electrostatic repulsion because the protonated adsorbent surface repel the cationic dye molecules. The adsorbent surface becomes positive after modification giving a pHpzc of 7.8 and the maximum removal occurred at pH 9. Beyond the pHpzc, the clay surface was negative and adsorption occurred by electrostatic attraction between the negative surface of adsorbent and cationic dye species. These results show that indeed the surface characteristics of the adsorbent influence its adsorption capacity.

As it has already been indicated earlier, anionic dye adsorption strongly depends on pH, and low pH ranges are ideal for their removal when metal oxides are used as sorbents (Afkhami and Moosavi, 2010; Saha et al., 2011). Hai et al. (2015) also obtained similar results in their study. These researchers used acid-activated kaolinite with TiO_2 to remove azo dyes CR, Direct Fast Scarlet 4BS (4BS), and weak acid dark blue 5R (5R)) from aqueous solution and like many dye removal studies, they also investigated the effect of pH to see how it will influence the percentage dye removal. Their findings showed that all the three dyes were maximally removed in acidic conditions than basic conditions. To explain their findings, the authors stated that pH determines TiO_2 nanoparticles surface charges and the ionic nature of dyes. Anirudhan and Ramachandran (2015) also gave the same explanation for dye adsorption earlier on. CR, 4BS, and 5R are anionic dyes and are negatively charged, it was quite expected that their removal be greater in acidic conditions and the results came out as expected. However, the same explanation cannot be given in the case of metal oxide adsorbents. The increased adsorption of the dyes on the metal oxide modified adsorbents under acidic conditions was mainly attributed to the electrostatic attraction between the negatively charged dye ions and the positively charged $Ti—OH_2^+$. On the contrary, under basic conditions, OH groups on the surface of TiO_2 dissociates forming TiO^- and therefore TiO_2 nanoparticles surfaces become negatively charged causing electrostatic repulsion between the dye anions and the negatively charged TiO^2 nanoparticles, resulting in a decrease in dye adsorption.

It is worth noting that it is not always the fact that adsorption processes always depend on pH, sometimes the adsorption may totally be independent of pH though this is not always the case for

Table 6
Comparison of adsorption properties of different clay composite materials.

Clay polymer nanocomposites	Dye	Enhancement action of polymer system	References
Poly (acrylamide-*co* acrylic acid)/Kaolinite P(AAm-AAc/Kao) Clay composite	Bromophenol Blue	An increase in temperature resulted in increase in the amount of BPB dye adsorbed per unit mass of sorbents	El-Zahhar et al. (2014)
Chitosan/Modified Ball (MBC-CH) Clay composite	Methylene Blue	Adsorption of MB on MBC–CH was found to increase as the initial concentration, solution pH and temperature of the solution were increased.	Auta and Hameed (2014)
Poly(ethylene glycol-*co*-acrylic acid)/Bentonite Clay nanocomposite semi-IPN type hydrogel	Congo Red and Methyl Violet	The nanocomposites showed high adsorption capacity and removal-% of CR and MV at a solution pH of 7	Bhattacharyya and Kumar-Ray (2015)
Poly(Acrylamide)/k-Carrageenin/Sodium Alginate Sodium Montmorillonite (MMT) Clay hydrogel nanocomposite	Crystal Violet	Dye adsorption capacity of hydrogels was influenced by both clay content and biopolymers weight ratio. At acidic media, the dye adsorption capacity of nanocomposites was enhanced as the carrageenan and clay content were increased.	Reza-Mahdavinia et al. (2013)
Poly(acrylicacid)/Bentonite/FeCo particles (PAAc-BFeCo) hybrid hydrogel nanocomposite	Crystal Violet	Exfoliated bentonite clay and Fe–Co particles increased the strength and stability of hydrogel and assisted the adsorption of CV	Shirsath et al. (2011)
CarAlg/MMt nanocomposite hydrogels	crystal violet	The adsorption capacity of nanocomposites was enhanced as the clay content was increased.	Mahdavinia et al. (2013)
kappa-carrageenan-*g*-poly(acrylamide)/sepiolite nanocomposite hydrogels	crystal violet	The speed of adsorption of cationic CV dye onto obtained hydrogels was improved by introducing sepiolite nanoclay.	Mahdavinia and Asgari (2013)
Novel kappa-carrageenan/poly (vinyl alcohol)/ montmorillonite nanocomposite hydrogels	Crystal violet	Compared with clay-free hydrogel, the nanocomposites indicated a relatively improved adsorption capacity at the same batch system.	Hosseinzadeh et al. (2015)
Magnetic carboxymethyl chitosan-gpoly(acrylamide)/laponite RD nanocomposites	Crystal violet	By introducing magnetic laponite RD, the nanocomposites showed an enhanced adsorption capacity for CV dye.	Mahdavinia and Karami (2015)
carrageenan-based nanocomposite superabsorbents	Crystal violet	The rate of dye adsorption is enhanced by increasing the clay content up to 14 wt% of clay.	Mahdavinia et al. (2012a)
Novel carrageenan-based hydrogel nanocomposites containing laponite RD		The effect of carrageenan and clay contents on the speed of dye adsorption revealed that while the rate of dye adsorption is enhanced by increasing the clay content, it was depressed as the carrageenan content increased in nanocomposites composition.	Mahdavinia et al. (2012b)

most studies. Santos et al. (2016) evaluated the effect of pH on Basic Red 46 uptake by bentonite clay. Contrary to the usual findings on the effect of pH on dye removal, their results show that the amount of adsorbed dye was not considerably affected by pH. They reported that, for initial pH values between 2 and 6, the BR adsorbed amount was approximately 220 mg/g and pH did not have a considerable impact on that adsorption capacity. Chemical adsorbent characterization before the dye adsorption experiments showed that 0.1, 0.01 and 0.001 mol/L, NaCl concentrations recorded the PZNPC of the adsorbent as 9.6, 9.9 and 10.1 respectively. Considering those PZNPC results, at low pH values, there is a positive pH-dependent charge meaning that it is only the negative permanent constant charge that is in charge for BR adsorption. As pH was increased an increase of adsorption capacity from 220 mg/g at pH 6–319 mg/g at pH 10 was observed and in that basic solution, equilibrium pH values ranging from 8.7 to 9.3 and those values were closely similar to PZNPC values. The negative pH-dependent charge and the permanent charge, plays a pivotal role in the improved adsorption capacity. Similar tendencies were also reported for the cationic dye adsorption by montmorillonite and palygorskite (Al-Futaisi et al., 2007; Roulia and Vassiliadis, 2008). These findings clearly indicates that BR dye (a cationic dye) can be taken up extensively even under unfavourable (acidic) conditions and furthermore bentonite clay did not show the weakness of being strongly dependent on pH to perform well.

7.2. *Effect of adsorbent dose*

To determine a minimum adsorbent dosage that is economically viable in wastewater treatment processes, many studies have investigated the effectiveness of several sorbent dosages on the removal both anionic and cationic dyes (Anirudhan and Ramachandran, 2015; Chaari et al., 2015; Yan et al., 2015). Generally, the percentage removal of dye is directly proportional to the adsorbent dosage (as the adsorbent dosage increases, the percentage removal of the dye also increases). A possible explanation for such a trend is that, with increase in adsorbent dosage, adsorption sites that can take up dye ions become more available. When the adsorbent dosage is low the adsorption rate is quick because of the readily available active sites and when the adsorbent dosage is high, the dye ions cannot readily access the adsorption sites easily until the attainment of equilibrium (Sarma et al., 2016).

Acid Blue 25 (AB25), Acid Blue 93 (AB93), Acid Golden Yellow G (AGYG) and Acid Turquoise Blue A (ATBA were used as model dyes in a study by Yan et al. (2015). Raw bentonite and CTMAB-Bentonite were used to test the effect of adsorbent dosage for this particular study. As expected, the results followed the general trend with adsorbent dosage. Their findings revealed that the amount of dye uptake increased with the increasing amount of the modified adsorbent. An 80% removal was achieved for AB93 and AB25 with a 0.02 g dosage. For the other 2 dyes, there was a rapid adsorption, with the equilibrium state being achieved at 0.05 g. All four dyes recorded more than 88% removal with the modified clay, while for raw bentonite the percentage removals were all lower than 30%. The findings showed that the adsorption ability of CTMAB-Bent was strongly enhanced by surfactant modification, by changing the hydrophilic surface to hydrophobic. A similar trend of results was also reported by Chaari et al., 2015 on the interactions of C.I. direct orange 34 (DO34) with Tunisian raw clay. To assess the adsorption capability of the clay, the dosage was varied in the range 0.3–1.5 g/

L. The percent removal improved from 87 to 85% with dose increase from 0.3 to 1 g/L. The authors reported that this might have been ascribed to an improved surface area of the adsorbent and the availability of additional adsorption sites. Nonetheless, above 1 g/L dose, there was a reduction in dye adsorption, which might have been caused by the reduction of the available surface area due to the formation of agglomerates by the clay minerals thereby blocking some of the binding sites.

Rehman et al. (2013) are also among many researchers that investigated the adsorbent dose effect on dye removal and they also acknowledge that it is important to select a proper initial adsorbent dosage because it controls adsorption by way of available adsorption sites and surface area (Javaid et al., 2011; Safa and Bhatti, 2011). These authors studied the removal of Brilliant Green dye by red clay (RC) and they varied the adsorbent dosage between 0.3 and 1.5 g/L. Their results showed an inverse relationship between removal efficiency and adsorbent dosage. Dye adsorption rose from 67% to 94%, while the adsorption capacity declined from 117.3 to 31.4 mg/g at a dose of 0.3–1.5 g/L. Mane and Babu (2011) and Safa and Bhatti (2011) also described a similar performance of adsorption against adsorbent amount. Increasing the amount of RC increases the available adsorption sites up to a particular level against a fixed dye molecules number (Ghaedi et al., 2011).

7.3. Effect of initial dye concentration

To evaluate the amount of dye adsorbed and consequentially the percentage of dye removed from a solution, investigating effect of the initial dye concentration becomes imperative. Previous studies have shown a general trend wherein increasing the initial dye concentration leads to a decrease in the percentage of dye removal (Anirudhan and Ramachandran, 2015; Yu et al., 2015). Various authors have attributed this to the saturation of adsorption sites on the sorbent surface by the adsorbate species. The percentage of dye adsorption rises with increasing contact time at all initial dye concentrations (Dawood and Sen, 2014). What happens is that a driving force to overcome the resistance to the mass transfer of dye is provided by the initial dye concentration between the aqueous and the solid phase (Rafatullah et al., 2010).

This phenomenon of saturation of sorption sites on the sorbent surface by the adsorbate species was also observed by Ogunmodede et al. (2015). They studied the removal of acid dye from using a combination of bentonite and kaolin clay and among other variables, also investigated the effect of initial dye concentration on dye uptake. The adsorption efficiency of kaolin-bentonite improved as the initial dye concentration increased. The authors suggested that increasing the dye concentration leads to a rise in mass gradient between the adsorbent and solution, hence acting as a driver to transfer the dye ions from bulk solution to the particle surface. An increase in the proportional dye adsorption was attributed to the equilibrium shift during the clay adsorption process (Ogunmodede et al., 2015). A different study by Makhoukhi et al., 2015 also revealed that the amount of dye adsorbed increased with increasing dye concentration up to a saturation level. Makhoukhi et al. (2015) reported on Telon dyes adsorption by bis-imidazolium modified bentonite from aqueous solutions and their findings showed that all organo-Bt adsorbents showed improved capacities for dyes retention.

Rehman et al. (2013) also did a study on the uptake of BG by red clay (RC) and reported that the adsorption process was directly proportional to the initial dye concentration because it drove the mass transfer rate under a higher concentration gradient between the RC surface and the dye solution. The same explanation has been reported by other studies including Aroguz et al. (2008) and Auta and Hameed (2012). Initial dye concentration effect (20–100 mg/L) on the adsorption of BG showed that adsorption efficiency and sorption capacity displayed opposite trends with increasing initial BG concentration. RC sorption capacity rose from 48 to 119.5 mg/g, while the adsorption efficiency declined from 96% to 47% with an increase in BG concentration from 20 mg/L to 100 mg/L, respectively. Numerous scholars similarly established comparable results using BG (Auta and Hameed, 2012, 2013; Nandi et al., 2009). Kismir and Aroguz (2011) revealed that the adsorption efficiency of BG by Saklikent mud improved with increasing initial BG concentration but their highest initial dye concentration used was 20 mg/L and it recorded a 96% removal. Auta and Hameed (2012; 2013) maintain that surfaces of the adsorbent have a fixed number of binding sites per unit mass of the sorbent. At lower initial dye concentration, the number of available sites is higher when compared to those at higher initial concentrations. As a result, majority of the dye ions are taken up by RC leading to greater percentage removal. Dye particles have to compete for the fixed number of adsorption sites at higher initial concentration hence some of dye particles cannot be taken up. The findings from the experiments confirmed that residual dye increased with the increase in initial dye concentration which resulted in lower adsorption efficacy (Nandi et al., 2009).

7.4. Effect of contact time

Researchers have done contact time studies to show a relationship between the amounts of dye adsorbed onto a fixed adsorbent mass with agitation/contact time (Chinoune et al., 2016; Elmoubarki et al., 2015; Fayazi et al., 2015; Santos and Boaventura, 2016). Contact time aids in finding the optimum time at which equilibrium is reached which can later on be applied in wastewater treatment plants based on wastewater process design. Contrary to other adsorption parameters, the effect of contact time does not have a definite general trend. However, most cases show that adsorption happens rapidly at the very first few minutes of contact and then proceeds gradually until equilibrium is reached after which the percentage removal of the dye will not change.

The same can be said for Safranin dye removal by magnetic mesoporous clay (MMC) reported by Fayazi et al. (2015). The effect of agitation time on the adsorbed amount of Safranin was studied from 0 to 90 min and the results revealed that dye removal took a two-stage process, with a fast initial Safranin adsorption followed by slow adsorption. It was clear that much of the dye molecules were adsorbed during the initial 10 min where the adsorption amount (qt) was about 10.7 mg/g and nearly levelling off after 10 min such that Safranin removal remained almost constant as contact time was increased. The authors suggested that the rapid initial uptake rate was due to the rapid diffusion of the dye from aqueous solution to the MMC composite external surface. Gradually occupation of the adsorption sites by Safranin dye occurs when dye molecules are transported from the bulk phase to the inner-sphere pores of MMC. At a later stage, the slow diffusion process decreased the adsorption rate and after 30 min of shaking, a steady equilibrium state could be considered.

A more or less similar trend of results was also obtained by Ogunmodede et al. (2015) who studied how contact time would affect the amount of CR taken up by kaolin-bentonite. Their findings indicated that when contact time is increased, the amount of dye taken up was not considerably increased. CR adsorption was very quick from the start of the experiments until around 50 min where a slight increase was observed until 80 min recording the maximum CR adsorption. It can be seen that above 80 min there was almost no change in the CR adsorption. Chaari et al. (2015) had a comparable observation concerning contact time effect on dye adsorption. The results of percent uptake of DO34 by HC was investigated at time intervals ranging from 5 to 90 min and the findings showed DO34 uptake increased with time until 60 min. Just like the other authors, the initial rapid adsorption was attributed to large number of adsorbent sites that were available for DO34 molecules and beyond 60 min, the adsorption capacity remained constant due to the saturation of adsorption sites. The overall conclusion on contact time studies is that adsorption occurs rapidly within the first few minutes of contact and then proceeds gradually until equilibrium is reached after which the dye percentage removal remains constant.

7.5. *Effect of temperature*

In order to determine if the adsorption process is going to occur in any adsorption process, energy and entropy values must be taken into consideration (Chen et al., 2011). The practical applicability of the process is indicated by thermodynamic parameter values. These parameters of thermodynamics on adsorption are usually obtained from the experimental data acquired at different temperatures (Chen et al., 2011). Evaluating thermodynamic parameters involves calculating the Gibbs free energy variation (ΔG), enthalpy variation (ΔH) and entropy (ΔS) according equations (1) and (2) (Yousef et al., 2011):

The standard free energy change **Δ**G is calculated using the following equation:

$$\Delta G = -RT \ln Ka \tag{1}$$

where ΔG is the free energy of sorption (kJ/mol), T is the temperature in Kelvin (K), R is the universal gas constant (8.314 J/mol/K) and Ka is the sorption equilibrium constant.

The sorption equilibrium constant Ka can be expressed in terms of enthalpy change (**Δ**H) and entropy change (**Δ**S) as a function of temperature and is shown below: (Alver and Metin, 2012; Ma et al., 2012).

$$\ln Ka = \frac{\Delta H}{RT} + \frac{\Delta S}{RT} \tag{2}$$

where ΔH is the heat of sorption (kJ/mol) and ΔS is the standard entropy change (kJ/mol/K).

The positive values of ΔH imply that the adsorption process is endothermic and it is an indication that the nature of the dye adsorption is predominantly physical, involving weak interaction forces. The positive values of ΔS suggest an improved chance of the solid to solution interface with some sorption system structural changes and an attraction to the adsorbate. Moreover, a positive ΔS value relates to a rise in the adsorbed species degree of freedom (Ma et al., 2012).

Temperature usually has a notable effect on reaction rate. If temperature increases, the rate of chemical reaction also increases (Mekatel et al., 2015). Hence the temperature of the aqueous solution has a vital role on the whole adsorption process. The increase or decrease of the adsorption capacity with temperature can help tell what type of adsorption took place. If the adsorption capacity increases with temperature then the adsorption is endothermic and if the adsorption capacity decreases with increasing temperature then the adsorption is an exothermic process (Zhao et al., 2013; Zulfikar, 2013; Khorramabadi et al., 2012). A number of investigations have shown that temperature plays an important role in the adsorption process (Anirudhan and Ramachandran, 2015; Chinoune et al., 2016; Rehman et al., 2013).

Elmoubarki et al., 2015 used Morrocan clays to adsorb MB, MG and MO from aqueous solution. These authors evaluated the temperature effect in a bid to test the capability of the clays to remove dyes from a variety of effluents, considering specific circumstances of dye wastewater. Accordingly they did data collection at five temperatures ranging from 10 to 50 °C. The quantities of MB, MG and MO adsorbed on the clays as function of the temperature of solution indicated that increasing solution temperature led to an increase of adsorbed MG. However, the adsorbed quantity of MO decreases significantly with an increase in temperature and lastly, the adsorption of MB was less influenced by temperature as the adsorbed amounts slightly decreases with the increase in solution temperature from 10 to 50 °C. Thermodynamic parameters results which include the change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were used to define the thermodynamic behaviour of the adsorption of MB, MG and MO onto the clays. From the calculated constants it was concluded that, the adsorption was exothermic in the case of MB and MO. To further determine the type of adsorption, the magnitude of enthalpies was calculated and the process recorded a decrease in entropy. The negative ΔS value suggested a decline in the randomness at the solid/solution interface during the adsorption. The Gibbs energy (ΔG) increased when the temperature was increased from 10 to 50 °C indicating a decrease in feasibility of adsorption at higher temperatures. In the case of MG, the adsorption was endothermic and accompanied by a decrease in ΔG values with the increase in temperature. The MG result indicated an increase in feasibility of adsorption at higher temperatures. The ΔS values were found to be positive which suggested an increase in the randomness at the solid/solution interface during the adsorption. From all this results, it could be concluded that adsorption of methyl orange was more influenced by the change in solution temperature.

Another study to examine the influence of temperature on dye uptake was carried out by Toor and Jin, 2012 using modified bentonite to remove diazo dye. They evaluated the effect of temperature on Congo Red (CR) adsorption on bentonite at 25, 30, 40, 50 and 60 °C. The temperature impact graph showed that as temperature was increased from 25 to 60 °C there was a minor decrease in the removal of CR. These findings revealed that the adsorption process was exothermic and lower temperatures favoured the adsorption process hence the negative H^o values. The change in enthalpy was found to be between −20 and 0 kJ mol^{-1}, indicating a physical reaction. From −400 to −80 kJ mol^{-1} chemisorption becomes predominant (Lian et al., 2009). Similar results were also reported by Vimonses et al. (2009) and Chatterjee et al. (2009). They argue that the decline in dye removal with rising temperatures is because of poor interaction between CR and bentonite because hydrogen bonds and Van der Waals are weak. Calculating the Gibbs energy gave negative values which is indicative of a spontaneous and feasible adsorption process. This further suggests that the adsorption of CR adsorption by modified clay does not considerable change internal structure of the clay. These findings were similar to those described by Ozcan et al. (2004) for the uptake of Acid Red 57 by acid activated bentonite. “The decrease in entropy implies the positive affinity of the adsorbents towards the CR adsorption” (Chatterjee et al., 2009).

7.6. *Effect of ionic strength*

Ionic strength is an important parameter to be investigated in adsorption experiments because it is well known that industrial wastewaters always have pollutants such as inorganic salts. The availability of such salts in solution leads to high ionic strength affecting the whole adsorption process at large (Anirudhan and Ramachandran, 2007). Usually, the variation of the concentration of salts like NaCl, KCl and $CaCl_2$ have a notable effect on the adsorption of acidic dyes. Most of the times, NaCl is used to stimulate the dying process. A study by Ma et al. (2013) to assess the removal of Congo Red, an acid dye using raw bentonite and surfactant-modified bentonite indicated that the adsorption of Congo Red, onto the negatively charged bentonite and positively charged CTABMBn was enhanced by adding the salts in the order: $NaCl < KCl < CaCl_2$. Ionic strength increase in solution may result in the compression of the diffuse double layer on the adsorbent thus easing the electrostatic attraction and the adsorption process consequently (Li et al., 2010; Peng et al., 2006).

Kamal et al. (2014) investigated the adsorption properties of PVA/PAA/clay composite hydrogel towards crystal violet. Among many of the parameters evaluated, the effect of NaCl concentration on the adsorption capacity of the PVA/PAA and PVA/PAA/clay composite hydrogels for CV dye was also studied. The findings show that the adsorption capacities of the adsorbent decreased with increasing NaCl concentration. The findings corroborate what was also reported by Bayramoglu et al. (2009). Generally what happens is that, as the ionic strength is increased with addition of NaCl, excessive Na^+ ions may screen the negatively charged adsorbent surfaces, leading to the reduction of electrostatic attractive force, and as a result, the cationic dye adsorption decreases. The authors concluded that NaCl addition deteriorates the performance of such prepared hydrogels for dye adsorption.

Fil et al. (2014) studied the effect of electrolyte concentrations on the removal of astrazon red violet (ARV) using montmorillonite. Unlike the above mentioned researchers who used different Cl salts, Fil et al. (2014) used different molar concentrations of NaCl solutions. The adsorption of ARV onto the montmorillonite surface was negatively affected by NaCl in aqueous solutions. Increasing the NaCl concentration from 0 mol/L - 0.1 mol/L, decreased the adsorption capacity from 194.12 mg/g to 179.05 mg/g. A possible explanation to this trend is that as ionic strength is increased electrostatic attraction between the adsorbate molecule and the adsorbent surface is reduced consequently reducing the removal efficiency. Ultimately, increasing solution ionic strength, also decreases the final pH of the suspension. As a result, positive ions increase at the montmorillonite surface, screening electrostatic interactions between charges and decreasing adsorption (Dogan et al., 2009; Weng et al., 2009).

Srivastava and Sillanpää (2016) studied the regeneration of a basic and an acidic dye on a clay nanocomposite. Desorption study showed that among all tested regenerants (0.5 mol/L HCl, NaOH, CH_3COOH, C_2H_5OH, 1:1 mixture of C_2H_5OH: HCl, acetone and ethylene glycol), acetone proved to be the highly efficient eluent by successfully desorbing the highest amount of dye from dye loaded adsorbent. Related results were also reported by other studies (Chowdhury et al., 2009; Dave et al., 2012). Accordingly, for further adsorption–desorption cycles, acetone was selected as a regeneration medium for the adsorbent. The regenerated sorbent was efficient for the removal of both dyes (>55%) for to two adsorption–desorption cycles. Nevertheless, the third cycle showed decreased adsorption to 44% and 48% respectively for CR and MB and as a result, further cycles were not investigated.

8. Process optimization

One of the major objectives of dye adsorption studies is finding the optimum process parameters to maximize the removal of dyes. To this aim, numerical optimization is employed to determine appropriate amounts or values needed for the different parameters to attain the maximum removal efficiency which is mostly measured as percentage removal (%). Table 7 summarizes the results of optimization conditions attained by different researchers on dye adsorption using various types of clays. Such results show the reliability of the applied model for the appraisal of real conditions (Hassani et al., 2015).

9. Adsorption isotherms

The adsorbate concentration in a solution is in dynamic equilibrium with the interface of the adsorbent. Analysing equilibrium data aids in the development of mathematical models which might be useful in the quantitative description of results. The equations together with the basic assumptions of these equilibrium models can predict the adsorption ions at the same time giving important data on the adsorption mechanisms. The Langmuir and Freundlich isotherms are the most common adsorption isotherm models applied in dye adsorption studies.

9.1. The Langmuir isotherm

The Langmuir isotherm model is based on the assumption that adsorption cannot proceed beyond the monolayer. It furthermore says that the adsorption of a particular molecule on a given adsorption does not depend on the occupation of the next adsorption site (Li et al., 2011).

Expressed mathematically by Equation (3) as,

$$\frac{Ce}{Qe} = \frac{1}{Qmb} \tag{3}$$

where Ce is the dye concentration at equilibrium (mg/L), Qe is the adsorbed amount of dye at equilibrium (mg/g), b represents the Langmuir isotherm constant and Qm is the maximum adsorption capacity for a total monolayer coverage.

9.2. The Freundlich isotherm

Contrary to the Langmuir isotherm, the Freundlich isotherm describes the adsorption characteristics for heterogeneous adsorbent surfaces (Singh et al., 2015).

Expressed mathematically by Equation (4) as,

$$\log Q_e = {}^{1}\!/_{n} \log\ C_e + \log\ K_F \tag{4}$$

K_F and $1/n$ are the Freundlich constants, describing the adsorption capacity and intensity respectively. The constants n and K_F are determined from the slope and the intercept respectively.

Researchers have used these two common adsorption isotherms to describe the mechanisms of dye adsorption onto various types of adsorbent surfaces. Chaari et al. (2015) applied the Langmuir and Freundlich isotherm models to study the mechanisms of adsorption of Direct Orange 34 (DO34) onto natural clay. The isotherms factors were evaluated at pH 3. By way of comparing correlation coefficients values (R^2) for the two isotherms, the Freundlich isotherm gave the best fitting model for the adsorption of DO34 onto halloysitic clay with a high correlation coefficient value of 0.99. This is indicative of adsorption of DO34 taking place on heterogeneous surfaces (Chaari et al., 2015). These results are also the same with those obtained by Yan et al. (2015). They also applied the Langmuir and the Freundlich models to their data on acid dyes adsorption by CTMAB modified bentonite from aqueous solution. Their findings showed that the Freundlich model gave the best fit having an R^2 vale of 0.93 compared to the Langmuir model which gave an R^2 value of 0.86. These results also corroborated with other studies on the adsorption of acid dyes by clays and organoclays (Hao et al., 2014; Hameed et al., 2007; Tümsek and Avci, 2013).

It is interesting to note that some data will however conform to the Langmuir isotherms more they will conform to the Freundlich indicating adsorption on homogenous surfaces. In another study by Abidi et al. (2015), equilibrium modelling was studied using Fouchana clay for the adsorption of Reactive Red 120 dye in the

Table 7
Optimum conditions of dye adsorption using various clays.

Clay	Dye	Experimental conditions	Optimised conditions	References
Red clay	Brilliant Green dye	pH (2–10), particle size (58–150 μm), adsorbent dose (0.3–1.5 g), contact time (5–1500 min), initial dye concentration (20–100 mg/L), and temperature (25–65 °C)	pH = 7, contact time = 240 min, dose = 0.4 g, initial dye concentration = 20 mg/L, particle size = 58 μm and temperature = 45 °C.	Rehman et al. (2013)
Surfactant modified bentonite clay (organoclay)	Basic dyes	0.1 g of organoclay with 50 mL of various dye solutions (200–1000 mol/L) and time up to 4 h.	pH = 9.0 temperature = 30 °C. contact time = 240 min.	Anirudhan and Ramachandran (2015)
Natural clay	Direct orange 34	pH (2–8), contact time (5–90 min), and HC dose (0.3–1.5 g) and dye initial concentration (20–150 mg/L).	pH = 6.61 contact time = 60 min and dose = 1 g,	Chaari et al. (2015)
Dirty bentonite	Reactive dyes	Dose (1–5 g) Temperature (278–313 K), initial dye concentration (20–120 mg/L) and pH (2–12).	Dose = 3 g, contact time = 180 min, pH = 2 and temperature = 298 K	Chinoune et al. (2016)
Alginate–clay quasi-cryogel beads	Methylene blue	Dose (2–10 mg/mL) Temperature (20–60 °C) and initial dye concentration (0.2–1.6 mg/mL)	Dose = 8 g, contact time = 100 min, temperature = 40 °C and initial dye concentration = 0.8 mg/mL.	Uyar et al., 2016
Modified natural bentonite	Diazo dye	pH (3–11), contact time (2–30 h), and HC dose (2–26 g) and initial dye concentration (100–1000 mg/L).	Dose = 14 g, contact time = 24 h, temperature = 40 °C and initial dye concentration = 1 L and pH > 10	Toor and Jin, 2012
Stevensite-rich Moroccan clay		Dose of 1 g/L, pH (3–10), Temperature (25, 45, and 55^{O}C) and initial dye (200–1000 mg/L)	Contact time = 2 h, temperature = 55 °C and initial dye concentration = 1 L and pH = 10	Elass et al., 2011
Magnetic mesoporous clay	Safranin dye	Contact time (0–90 min), dose (0.03 –0.07 g), pH (6–10), and initial dye concentration (40–80 mg/L)	Contact time = 30 min, temperature = low temperatures	Fayazi et al., 2015
Kaolin and Bentonite clay mixture		Contact time (1–80 min), pH (5–13), and initial dye concentration (75–300 mg/L)	Contact time = 50 min, initial dye concentration = 100 mg/L and pH = 10	Ogunmodede et al., 2015

presence of CHT-Catalase. The results were obtained from using the Langmuir and Freundlich isotherm models. In all cases, the Langmuir isotherm gave the best fit compared to the Freundlich isotherm. Data fitting best to the Langmuir isotherm indicates that in the presence of CHT Catalase, the dye alone forms a monolayer on the surfaces of Fouchana clay (Abidi et al., 2015). Chinoune et al. (2016) reported on the removal of reactive dyes by dirty bentonite from aqueous solution. In this case, the Langmuir isotherms R^2 values were found considerably higher than those of the Freundlich isotherms too. Since the Langmuir isotherms fitted the experimental data best it showed the presence homogenous distribution of active sites on the magnesium hydroxide coated bentonite, (B–$Mg(OH)_2$) surface. This conclusion is based on the fact that the Langmuir model assumes that adsorption takes place on homogenous surfaces. Another adsorption isotherm modelling study was also done Fayazi et al., 2015 and the Langmuir and Freundlich constants calculated and reported. The adsorption of Safranin was well fitted to the Langmuir isotherm model with the higher R^2 (0.98). It indicated the adsorption took place at specific homogeneous sites within the adsorbent forming monolayer coverage of Safranin on the surface of the absorbent.

10. Desorption studies

Even though some clays have high adsorption capacities with respect to the removal of dyes, the ability of the adsorbents to be regenerated is a crucial factor to assess their reusability. Regeneration of a spent adsorbent is usually carried out in order to reuse it, avoid the cost of a new acquisition and minimizing the amount of waste. Many researchers have investigated desorption of adsorbed dye using various types of eluents. Some adsorbents can be efficiently adsorbed and reused again for many times but unfortunately some adsorbents do not perform efficiently after desorption and some materials may be lost or their structures destroyed during the desorption process.

Mahdavinia et al. (2016) used ethanol (96% V/V), 0.5 M of KCl solution, 50/50 V/V of ethanol/water mixture and 0.5 M of KCl in 50/50 V/V of ethanol/water mixture to desorb dyes from spent nanocomposites. The use of the above mentioned solutions was ineffective for desorption purposes and therefore there was a need to try other different solutions. For more practical applications of the desorption study the authors attempted to desorb the dye via a mixture of ethanol/water and KCl. The spent adsorbents were desorbed by 0.5 M of KCl in ethanol/water leading to a desorption efficiency of more than 94%. Because of the successful desorption results, Mahdavinnia and coworkers decided to carry out 5 desorption– adsorption processes using the same regeneration agent. Throughout all the regeneration cycles, the nanocomposite mCarraLap3 showed a constant dye adsorption capacity and the change in desorption efficiency and adsorption capacity for all other composites was almost negligible. In actual fact, the findings showed that the nanocomposites could be used for multiple cycles without a decrease in adsorption capacity for CV dye.

To evaluate the regeneration of sepiolite clay and study the mechanisms involved in BR sorption, Santos and Boaventura (2016) carried out desorption experiments using NaOH and HCl as regeneration agents. Desorption studies conducted for BR-loaded sepiolite showed that the maximum BR desorbed percentage was 9.4% and it was obtained for strong acidic conditions (pH 2). For higher pH values, desorption was very low and limited to 2–3%, which reflects the establishment of strong chemical bonds between the basic dye and the sepiolite in the adsorption. The results showed no feasible regeneration by using acid or alkaline solutions. The reduced color leachability from the dye-loaded sepiolite is, on the other side, a good feature considering the disposal in landfill or reuse for other purposes, such as incorporation in construction materials or in polymeric composites (Zhou et al., 2014).

11. Conclusions

This review paper was mainly looking at the adsorption of different dyes onto various clay based adsorbents. Various materials are currently available to remove dyes from water, but clays are generally considered attractive because of their effectiveness, convenience, ease of operation, simplicity of design and for economic and environmental reasons. Performance comparison of different adsorbents is difficult because of inconsistencies in the data, principally due to different experimental conditions including pH, temperature, particle size and initial dye concentration. The review gave an extensive range of clay material adsorbents. From the literature review surveyed, it was shown that cheap, readily and locally available clay minerals could be used for effective dye adsorption from aqueous solution rather than the expensive commercial activated carbon. Low cost clay adsorbents offers quite a number of benefits that are applicable in the commercial world today and most probable a lot more in the near future. From the literature reviewed, chemically modified clay sorbents demonstrated exceptional adsorption abilities for various dyes when compared to raw clays. Regardless of a large amount of studies on clay adsorbents, there is little data containing a full study comparing the economic viability between these clay adsorbents. Even though a lot has been done on studies dealing with clay material sorbents, a great deal of work still needs to be done to predict the performance of the adsorption processes for dye adsorption in real world industrial effluents under various operating conditions and not only in the laboratory. At the present state of knowledge, it is necessary to continue investigating the potential of these natural adsorbent at and industrial scale and also their potential use after adsorption in various industries including brick manufacturing and landscaping. The benefit would be environmental by the valorisation on one hand, of the adsorbent, and on the other hand of the treated water, thus reducing the water demand. The use of these clay based alternative adsorbent would also bring economic advantages because of the low cost of the material, and potentially by its valorisation.

Acknowledgements

The authors wish to express their sincere gratitude to the University of Venda Research Directorate, Council for Scientific and Industrial Research (CSIR), Water Research Commission (WRC) and National Research Foundation (NRF) for supporting this project financially.

References

Abidi, N., Errais, E., Duplay, J., Trabelsi-Ayadi, M., 2015. Treatment of dye-containing effluent by natural clay. J. Clean. Prod. 86, 432–440.

Adensola, B., Ogundipe, K., Sangosanya, K.T., Akintola, B.D., Oluwa, A., Hassan, E., 2016. Comparative study on the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass (Cymbopogon citratus): kinetics, isotherms and thermodynamics. Chem. Int. 2, 89–102.

Adeyemo, A.A., Adeoye, I.O., Bello, O.S., 2015. Adsorption of dyes using different types of clay: a review. Appl. Water Sci. http://dx.doi.org/10.1007/s13201-015-0322-y.

Afkhami, A., Moosavi, R., 2010. Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. J. Hazard. Mater 174, 398–403.

Ajbary, M., Santos, A., Morales-Flórez, V., Esquivias, R., 2013. Removal of basic yellow cationic dye by an aqueous dispersion of Moroccan stevensite. Appl. Clay. Sci. 80–81, 46–51.

Ali, I., Asim, M., Khan, T.A., 2012. Low cost adsorbents for the removal of organic pollutants from wastewater. J. Environ. Manag. 113, 170–183.

Al-Futaisi, A., Jamrah, A., Ai-Hanai, R., 2007. Aspects of cationic dye molecule adsorption to palygorskite. Desalination 214 (1–3), 327–342.

Almeida, C.A.P., Debacher, N.A., Downs, A.J., Cottet, L., Mello, C.A.D., 2009. Removal of methylene blue from coloured effluents by adsorption on montmorillonite clay. J. Colloid Interface Sci. 332, 46–53.

Alver, E., Metin, A.U., 2012. Anionic dye removal from aqueous solutions using modified zeolite: adsorption kinetics and isotherm studies. Chem. Eng. J. 200–202, 59–67.

Ambasht, R., Sillanpa, M., 2010. Water purification using magnetic assistance: a review. J. Hazard Mater 180, 38–49.

Anirudhan, T.S., Ramachandran, M., 2007. Surfactant-modified bentonite as adsorbent for the removal of humic acid from wastewaters. Appl. Clay Sci. 35, 276–281.

Anirudhan, T.S., Ramachandran, M., 2015. Adsorptive removal of basic dyes from aqueous solutions by surfactant modified halloysite clay (organoclay): kinetic and competitive adsorption isotherm. Process Saf. Environ. Prot. 95, 215–225.

Auta, M., Hameed, B.H., 2012. Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue. Chem. Eng. J. 198–199, 219–227.

Auta, M., Hameed, B.H., 2013. Acid modified local clay beads as effective low-cost adsorbent for dynamic adsorption of methylene blue. J. Ind. Eng. Chem. 19, 1153–1161.

Auta, M., Hameed, B.H., 2014. Chitosan-clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. Chem. Eng. J. 237, 352–361.

Aroguz, A.Z., Gulen, J., Evers, R.H., 2008. Adsorption of methylene blue from aqueous solution on pyrolyzed petrified sediment. Bioresour. Technol. 99, 1503–1508.

Artioli, Y., 2008. Adsorption. In: Erik, Sven, Brian, F. (Eds.), Encyclopedia of Ecology. Academic Press, Oxford, pp. 60–65.

Avena, M.J., De Pauli, C.P., 1998. Proton adsorption and electrokinetics of an Argentinean montmorillonite. J. Colloid Interf. Sci. 202, 195–204.

Baskaralingam, P., Pulikesi, M., Elango, D., Ramamurthi, V., Sivanesan, S., 2006. Adsorption of acid dye onto organobentonite. J. Hazard Mater 128, 138–144.

Babarinde, A., Onyiaocha, G.O., 2016. Equilibrium sorption of divalent metal ions onto groundnut (Arachis hypogaea) shell: kinetics, isotherm and thermodynamics. Chem. Int. 2, 37–46.

Balik, O.Y., Aydin, S., 2016. Coagulation/flocculation optimization and sludge production for pre-treatment of paint industry wastewater. Desalination Water Treat. 57, 12692–12699.

Bayramoglu, G., Altintas, B., Arica, M.Y., 2009. Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin. Chem. Eng. J. 152, 339.

Benefield, D., Larry, D., Judkins, Joseph F., Barron, L., 1982. Process Chemistry for Water and Wastewater Treatment. Prentice hall, Englewood cliffs, New Jersey.

Bilal, N., Ali, S., Iqbal, M., 2014. Application of advanced oxidations processes for the treatments of textile effluents. Asian J. Chem. 26, 1882–1886.

Bhattacharyya, R., Kumar-Ray, S., 2015. Removal of Congo red and methyl violet from water using nano clay filled composite hydrogels of poly acrylic acid and polyethylene glycol. Chem. Eng. J. 260, 269–283.

Bohor, B.F., Randall, H.E., 1970. Scanning Electron Microscopy of Clays and Clay Minerals. Illinois State Geological Survey, Natural Resources Building, Urbana, Ill. 61801.

Boyd, S.A., Mortland, M.M., Chiou, C.T., 1998. Sorption characteristic of organic compounds on hexadecyltrimethylammonium-smectite. Soil Sci. Soc. Am. J. 52, 652–657.

Buthelezi, S.P., Olaniran, A.O., Pillay, B., 2012. Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates. Molecules 17, 14260–14274.

Bujdák, J., Komadel, R., 1997. Interaction of methylene blue with reduced charge montmorillonite. J. Phys. Chem. B 101, 9065–9068.

Bujdák, J., Chorvát, D., Iyi, N., 2010. Resonance energy transfer between rhodamine molecules adsorbed on layered silicate particles. J. Phys. Chem. C 114, 1246–1252.

Cadena, F., Rizvi, R., Peters, R.W., 1990. Feasibility studies for the removal of heavy metals from solution using tailored bentonite. In: Hazardous and Industrial Wastes Twenty-second Mid-Atlantic Industrial Waste Conference. Drexel University.

Cai, D.Q., Zhang, H., Tang, Y., Chu, P.K., Yu, Z.L., Wu, Z.Y., 2010. Nano-networks have better adsorption capability than nano-rods. Nano Commun. Netw. 1, 257–263.

Ceyhan, O., Baybas, D., 2001. Adsorption of some textile dyes by hexadecyltrimethylammonium bentonite. Turk J. Chem. 25, 193–200.

Chaari, I., Moussi, B., Jamoussi, F., 2015. Interactions of the dye, C.I. direct orange 34 with natural clay. J. Alloys Compd. 647, 720–727.

Chapman, A.C., Siebold, A., 1912. On the application of adsorption to the detection and separation of certain dyes. Analyst 37, 339–345.

Chatterjee, S., Lee, D.S., Lee, M.W., Woo, S.H., 2009. Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with nonionic or anionic surfactants. Bioresour. Technol. 100, 3862–3868.

Cheknane, B., Bouras, O., Baudu, M., Basly, J.P., Cherguielaine, A., 2010. Granular inorgano–organo pillared clays (GIOCs): preparation by wet granulation, characterization and application to the removal of a Basic dye (BY28) from aqueous solutions. Chem. Eng. J. 158, 528–534.

Cheknane, B., Baudu, M., Basly, J., Bouras, O., Zermane, F., 2012. Modeling of basic green 4 dynamic sorption onto granular organo–inorgano pillared clays (GOICs) in column reactor. Chem. Eng. J. 209, 7–12.

Chen, D., Chen, J., Luan, X., Ji, H., Xia, Z., 2011. Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange. Chem. Eng. J. 171, 1150–1158.

Chen, D.M., Chen, J., Wang, X.M., Luan, X.L., Ji, H.P., Xu, F., 2011a. Adsorption of methylene blue from aqueous solution by anionic surfactant modified montmorillonite. Adv. Mater. Res. 178, 29–34.

Chen, H., Zhao, J., Zhan, A.G., Jin, Y.X., 2011b. Removal capacity and adsorption mechanism of heat-treated palygorskite clay for methylene blue. Chem. Eng. J. 174, 143–150.

Chen, D., Chen, J., Luan, X., Zhiguo, X., 2016. Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange. Chem. Eng. J. 171 (3), 1150–1158.

Chinoune, K., Bentale, K., Bouberka, Z., Nadim, A., Maschke, U., 2016. Adsorption of reactive dyes from aqueous solution by dirty bentonite. Appl. Clay Sci. 123, 64–75.

Chollom, M.N., 2014. Treatment and Reuse of Reactive Dye Effluent from Textile Industry Using Membrane Technology. A thesis submitted in fulfilment of the academic requirements for the degree of Master of Technology in Engineering Durban University of Technology.

Chowdhury, A.K., Sarkar, A.D., Bandyopadhyay, A., 2009. Rice husk ash as a low cost adsorbent for the removal of methylene blue and Congo red in aqueous phases. Clean Soil Air Water 37, 581–591.

Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal: a review. Bioresour. Technol. 97, 1061–1085.

Daneshvar, N., Oladegaragoze, A., Djafarzadeh, N., 2006. Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters. J. Hazard Mater 129, 116–122.

Dave, S., Dave, V., Tipre, D., 2012. Coconut husk as a biosorbent for methylene blue removal and its kinetics study. Adv. Environ. Res. 1, 223–236.

Dawood, S., Sen, T., 2014. Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. J. Chem. Process Eng. 1, 104.

Diaz, F.R., Santos, P., 2010. Studies on the acid activation of Brazilian smectitic clay. Quim. Nova 24, 345–353.

Dogan, M., Karaoglu, M.H., Alkan, M., 2009. Adsorption kinetics of maxilon yellow 4GL and maxilon red GRL dyes on kaolinite. J. Hazard. Mater 165, 1142–1151.

Drouiche, N., Aoudj, S., Hecini, M., Ouslimane, T., 2011. Experimental design for the elimination of fluoride from pretreated photovoltaic wastewater by electrocoagulation. Chem. Eng. Trans. 24, 1207–1212.

Elass, K., Laachach, A., Alaoui, A., Azzi, M., 2011. Removal of methyl violet from aqueous solution using a stevensite-rich clay from Morocco. Appl. Clay Sci. 54, 90–96.

Elmoubarki, R., Mahjoubi, F.Z., Tounsadi, H., Moustadraf, J., Abdennouri, M., Zouhri, A., ElAlban, A., Barka, N., 2015. Adsorption of textile dyes on raw and decanted Moroccan clays: kinetics, equilibrium and thermodynamics. Water Resour. Industry 9, 16–29.

El-Zahhar, A.A., Awwad, N.S., El-Katori, E.E., 2014. Removal of bromophenol blue dye from industrial waste water by synthesizing polymer-clay composite. J. Mol. Liq. 199, 454–461.

Errais, E., Duplay, J., Elhabiri, M., Khodja, M., Ocampo, R., 2012. Anionic RR120 dye adsorption onto raw clay: surface properties and adsorption mechanism. Colloids Surf. A Physicochem. Eng. Asp. 403, 69–78.

Eren, E., 2010. Adsorption performance and mechanism in binding of azo dye by raw bentonite. Clean Soil Air Water 38, 758–763.

Espantaleon, A.G., Nieto, J.A., Fernandez, M., Marsal, A., 2003. Use of activated clays in the removal of dyes and surfactants from tannery waste waters. Appl. Clay Sci. 24, 105–110, 69, 310–314.

Fan, L., Zhang, Y., Luo, C., Lu, F., Qiu, H., Sun, M., 2012. Synthesis and characterization of magnetic -cyclodextrin-chitosan nanoparticles as nano-adsorbents for removal of methyl blue. Int. J. Biol. Macromol. 50, 444–450.

Fayazi, M., Afzali, D., Taher, M.A., Mostafavi, A., Gupta, V.K., 2015. Removal of Safranin dye from aqueous solution using magnetic mesoporous clay: optimization study. J. Mol. Liq. 212, 675–685.

Fil, B.A., Yilmaz, M.T., Bayar, S., Elkoca, M.T., 2014. Investigation of adsorption of the dyestuff astrazon red violet 3rn (basic violet 16) on montmorillonite clay. Braz. J. Chem. Eng. 31 (1). http://dx.doi.org/10.1590/S0104-66322014000100016.

Fosso-Kankeu, E., Waanders, F., Fraser, C., 2014. Bentonite clay adsorption affinity for anionic and cationic dyes. In: 6th Int'l Conf. on Green Technology, Renewable Energy & Environmental Engg. Cape Town (SA).

Frini-Srasra, N., Srasra, E., 2009. Adsorption of quinalizarin from non-aqueous solution onto acid activated palygorskite. Surf. Eng. Appl. Electrochem 45, 306–311.

Gao, Q., Luo, J., Wang, X., 2015. Novel hollow α-Fe$_2$O$_3$ nanofibers via electrospinning for dye adsorption. Nanoscale Res. Lett. 10, 1–8.

Ge, F., Ye, H., Li, M.M., Zhao, B.X., 2012. Efficient removal of cationic dyes from aqueous solution by polymer-modified magnetic nanoparticles. Chem. Eng. J. 198–199, 11–17.

Ghaedi, M., Hossainian, H., Montazerozohori, M., Shokrollahi, A., Shojaipour, F., Soylak, M., Purkait, M.K., 2011. A novel acorn based adsorbent for the removal of brilliant green. Desalination 281, 226–233.

Ghosh, R.K., Reddy, D.D., 2014. Crop residue ashes as adsorbents for basic dye (methylene blue) removal: adsorption kinetics and dynamics. Clean. Soil Air Water 42 (8), 1098–1105.

Giakisikli, G., Anthemidis, A., 2013. Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation: a review. Anal. Chim. Acta 789, 1–16.

Gomes, R.F., de Azevedo, A.C.N., Pereira, A.G.B., Muniz, E.C., Fajardo, A.R., Rodrigues, F.H.A., 2015. Fast dye removal from water by starch-based nanocomposites. J. Colloid Interface Sci. 454, 200–209.

Greenwood, R., Kendall, K., 1999. Selection of suitable dispersants for aqueous suspensions of Zirconia and Titania powders using acoustophoresis. J. Eur. Ceram. Soc. 19 (4), 479–488.

Grim, R.E., 1962. Applied Clay Mineralogy. McGraw-Hill, New York.

Gupta, V.K., Kumar, R., Nayak, A., Saleh, T.A., Barakat, M.A., 2013. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv. Colloid Interface Sci. 193, 24–34.

Hai, Y., Li, X., Wu, H., Zhao, S., Deligeer, W., Asuha, S., 2015. Modification of acid-activated kaolinite with TiO$_2$ and its use for the removal of azo dyes. Appl. Clay Sci. 114, 558–567.

Hajjaji, W., Pullar, R.C., Labrincha, J.A., Rocha, F., 2016. Aqueous Acid Orange 7 dye removal by clay and red mud mixes. Appl. Clay Sci. 126, 197–206.

Hao, Y., Yan, L., Yu, H., Yang, K., Yu, S., Shan, R., Du, B., 2014. Comparative study on adsorption of basic and acid dyes by hydroxy-aluminum pillared bentonite. J. Mol. Liq. 199, 202–207.

Han, Z.X., Zhu, Z., Wu, D.D., Wu, J., Liu, Y.R., 2014. Adsorption kinetics and thermodynamics of acid blue 25 and methylene blue dye solutions on natural sepiolite. Synth. React. Inorg. Met. 44, 140–147.

Hanaor, D.A.H., Michelazzi, M., Leonelli, C., Sorrell, C.C., 2012. The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO$_2$. J. Eur. Ceram. Soc. 32 (1), 235–244.

Hameed, B.H., Ahmad, A.A., Aziz, N., 2007. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. Chem. Eng. J. 133, 195–203.

Hassani, A., Khataee, A., Karaca, S., Karaca, S., Kıranşana, M., 2015. Adsorption of two cationic textile dyes from water with modified nanoclay: a comparative study by using central composite design. J. Environ. Chem. Eng. 3, 2738–2749.

Hashem, F.S., 2013. Removal of methylene blue by magnetite covered bentonite nano-composite. Eur. Chem. Bull. 2 (8), 524–529.

Hashemian, S., 2010. MnFe$_2$O$_4$/bentonite nano composite as a novel magnetic material for adsorption of acid red 138. Afr. J. Biotech. 9 (50), 8667–8671.

Heinz, R.A., Vaia, R., Krishnamoorti, B.L., 2007. Farmer, Self-assembly of alkylammonium chains on montmorillonite: effect of chain length, head group structure, and cation exchange capacity. Chem. Mater 19, 59–68.

Hosseinzadeh, H., Zoroufi, S., Mahdavinia, G.R., 2015. Study on adsorption of cationic dye on novel kappa-carrageenan/poly(vinyl alcohol)/montmorillonite nanocomposite hydrogels. Polym. Bull. 72, 1339–1363. http://dx.doi.org/10.1007/s00289-015-1340-5.

Huang, R., Wang, B., Yang, B., Zheng, D., Zhang, Z., 2011. Equilibrium, kinetic and thermodynamic studies of adsorption of Cd (II) from aqueous solution onto HACC-bentonite. Desalination 280, 297–304.

Hunger, K., 2003. Industrial Dyes, Chemistry, Properties, Applications. KGaA, WILEY-VCH Verlag GmbH & Co, Weinheim.

Iqbal, M., Ahmad, I., Bhatti, I.A., 2014. Re-utilization option of industrial wastewater treated by advanced oxidation process. Pak. J. Agri. Sci 51 (4), 1041–1047.

Izuagie, A.A., Gitari, W.M., Gumbo, J.R., 2016. Synthesis and performance evaluation of Al/Fe oxide coated diatomaceous earth in groundwater defluoridation: towards fluorosis mitigation. J. Environ. Sci. Health Part A 1–15.

Jaafar, S.N.B., 2006. Adsorption Study – Dye Removal Using Clay. An honors thesis submitted to the University College of Engineering & Technology Malaysia.

Jamal, M.A., Muneer, M., Iqbal, M., 2015. Photo-degradation of monoazo dye blue 13 using advanced oxidation process. Chem. Int. 1, 12–16.

Javaid, M., Saleemi, A.R., Naveed, S., Zafar, M., Ramzan, N., 2011. Anaerobic treatment of desizing effluent in a mesophilic anaerobic packed bed reactor. JPIChE 39, 61–67.

Jovic-Jovicic, N., Milutinovic-Nikolic, A., Grzetic, I., Jovanovic, D., 2008. Organo-bentonite as efficient textile dye sorbent. Chem. Eng. Technol. 31, 567–574.

Kalibantonga, P.D., 2004. Adsorption of Heavy Metals from Solution by South African Industrial Clay. A thesis submitted at Tshwane University of Technology.

Kamal, H., El-Sayed, A., Sabaa, M.W., Maher, El-Dessouky M., Mohamed, M.M., 2014. Adsorption properties of PVA/PAA/clay composite hydrogel synthesized by Gamma radiation and its application in removal of crystal violet dye from its aqueous solution. J. Nucl. Tech. Appl. Sci. 2 (5), 523–537.

Kant, R., 2012. Adsorption of dye eosin from an aqueous solution on two different samples of activated carbon by static batch method. J. Water Resour. Prot. 4, 93–98.

Kavitha, D., Namasivayam, C., 2007. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon.Bioresour. Technol 98, 14–21.

Khan, T., Khan, E., Shahjahan, 2015. Removal of basic dyes from aqueous solution by adsorption onto binary iron-manganese oxide coated kaolinite: non-linear isotherm and kinetics modeling. Appl. Clay Sci. 107, 70–77.

Khorramabadi, G.S., Soltani, R.D.C., Rezaee, A., Khataee, A.R., Jafari, A.J., 2012. Utilisation of immobilised activated sludge for the biosorption of chromium (VI). Can. J. Chem. Eng. 90, 1539.

Kismir, Y., Aroguz, A.Z., 2011. Adsorption characteristics of the hazardous dye Brilliant Green on Saklıkent mud. Chem. Eng. J. 172, 199–206.

Kobya, M., Bayramoglu, M., Eyvaz, M., 2007. Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections. J. Hazard Mater 148, 311–318.

Kono, H., 2015. Preparation and characterization of amphoteric cellulose hydrogels as adsorbents for the anionic dyes in aqueous solutions. Gels 1, 94–116.

Lazarević, S., Janković-Častvan, I., Jovanović, D., Milonjić, S., Janaćković, D., Petrović, R., 2007. Adsorption of Pb^{2+}, Cd^{2+}, and Sr^{2+} ions onto natural and acid-activated sepiolites. Appl. Clay Sci. 37, 47–57.

Lazarević, I., Janković-Častvan, V., Djokić, Z., Radovanović, D., Janaćković, R., Petrović, J., 2010. Iron-modified sepiolite for Ni^{2+} sorption from aqueous solution: an equilibrium, kinetic, and thermodynamic study. Chem. Eng. Data 55, 5681–5689.

Li, Q., Yue, Q.Y., Sun, H.J., Su, Y., Gao, B.Y., 2010. A comparative study on the properties, mechanisms and process designs for the adsorption of non-ionic or anionic dyes onto cationic-polymer/bentonite. J. Environ. Manag. 91, 1601–1611.

Li, M., Yao, J., Lin, B., Yang, X., Zhang, L., Lei, L., 2013. Pentachlorophenol sorption in the cetyltrimethylammonium bromide/bentonite one-step process in single and multiple solute systems. J. Chem. Eng. Data 58, 2610–2615.

Liu, P., Zhang, L., 2007. Adsorption of dyes from aqueous solutions of suspensions with clay nano-adsorbents. Sep. Purif. Technol. 58, 32–39.

Li, Z., Chang, P., Jiang, W., Jean, J., Honga, H., 2011. Mechanism of methylene blue removal from water by swelling clays. Chem. Eng. J. 168, 1193–1200.

Li, C., Huang, B., Li, C., Chen, X., Huang, Y., 2016. In situ formation of nanoscale zero-value iron on fish-scale-based porous carbon for Cr(VI) adsorption. Water Sci. Technol. 74 (11) http://dx.doi.org/10.2166/wst.2016.077.

Liu, M., Li, W., Rong, J., et al., 2012. Novel polymer nanocomposite hydrogel with natural clay nanotubes. Colloid Polym. Sci. 290, 895. http://dx.doi.org/10.1007/s00396-012-2588-z.

Lian, L., Guo, L., Guo, C., 2009. Adsorption of Congo red from aqueous solution on Cabentonite. J. Hazard. Mater 161, 126–131.

Liang, X., Xu, Y., Tan, X., Wang, L., Sun, Y., Lin, D., Sun, Y., Qin, X., Wang, Q., 2013. Heavy metal adsorbents mercapto and amino functionalized palygorskite: preparation and characterization. Colloids Surf. A 426, 98–105.

Liu, H., Chen, W., Liu, C., Liu, Y., Dong, C., 2014. Magnetic mesoporous clay adsorbent: preparation, characterization and adsorption capacity for antrazine. Microporous Mesoporous Mater 194, 72–78.

Liu, Y., Wang, W.B., Wang, A.Q., 2012. Effect of dry grinding on the microstructure of palygorskite and adsorption efficiency for methylene blue. Powder Technol. 225, 124–129.

Lv, G., Li, Z., Jiang, W., Chang, P., Jean, J., Lin, K., 2011. Mechanism of acridine orange removal from water by low-charge swelling clays. Chem. Eng. J. 174, 603–611.

Ma, A., Youssef, A.M., Al-Awadhi, M.M., 2013. Adsorption of acid dyes onto bentonite and surfactant-modified bentonite. J. Anal. Bioanal. Tech. 4, 174. http://dx.doi.org/10.4172/2155-9872.1000174.

Ma, J., Jia, Y., Jing, Y., Yao, Y., Sun, J., 2012. Kinetics and thermodynamics of methylene blue adsorption by cobalt-hectorite composite. Dyes Pigm. 93, 1441–1446.

Mahdavinia, G.R., Aghaie, H., Sheykhloie, H., Vardini, M.T., Etemadi, H., 2013. Synthesis of CarAlg/MMt nanocomposite hydrogels and adsorption of cationic crystal violet. Carbohydr. Polym. 98, 358–365.

Mahdavinia, G.R., Asgari, A., 2013. Synthesis of kappa-carrageenan-g-poly(-acrylamide)/sepiolite nanocomposite hydrogels and adsorption of cationic dye. Polym. Bull. 70, 2451. http://dx.doi.org/10.1007/s00289-013-0966-4.

Mahdavinia, G.R., Karami, S., 2015. Synthesis of magnetic carboxymethyl chitosan-gpoly(acrylamide)/laponite RD nanocomposites with enhanced dye adsorption capacity. Polym. Bull. 72, 2241–2262. http://dx.doi.org/10.1007/s00289-015-1402-8.

Mahdavinia, G.R., Massoumi, B., Jalili, K., Kiani, G., 2012a. Effect of sodium montmorillonite nanoclay on the water absorbency and cationic dye removal of carrageenan-based nanocomposite superabsorbents. J. Polym. Res. 19, 9947. http://dx.doi.org/10.1007/s10965-012-9947-9.

Mahdavinia, G.R., Massoudi, A., Baghban, A., et al., 2012b. Novel carrageenan-based hydrogel nanocomposites containing laponite RD and their application to remove cationic dye. Iran Polym. J. 21, 609. http://dx.doi.org/10.1007/s13726-012-0066-6.

Mahdavinia, G.R., Zhale, R., Baghy, R., 2012c. Removal kinetic of cationic dye using poly (sodium acrylate)-carrageenan/Na-montmorillonite nanocomposite superabsorbents. J. Mater. Environ. Sci 3 (5), 895–906.

Mahdavinia, G.R., Rahmani, Z., Mosallanezhad, A., Karami, S., Shahriari, M., 2016. Effect of magnetic laponite RD on swelling and dye adsorption behaviors of κ-carrageenan-based nanocomposite hydrogels. Desal. Water Treat. 57 (43), 20582–20596. http://dx.doi.org/10.1080/19443994.2015.1111808.

Makarchuk, O.V., Dontsova, T.A., Astrelin, I.M., 2016. Magnetic nanocomposites as efficient sorption materials for removing dyes from aqueous solutions. Nanoscale Res. Lett. 11 (161) http://dx.doi.org/10.1186/s11671-016-1364-2.

Makhoukhi, B., Djab, M., Didi, M.A., 2015. Adsorption of Telon dyes onto bis-imidazolium modified bentonite in aqueous solutions. J. Environ. Chem. Eng. 3, 1384–1392.

Mane, V.S., Babu, P.V.V., 2011. Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust. Desalination 273, 321–329.

Masindi, V., Gitari, W.M., Ngulube, T., 2014. Defluoridation of drinking water using Al^{3+} -modified bentonite clay: optimization of fluoride adsorption conditions. Toxicol. Environ. Chem. 96 (9), 1294–1309.

Masindi, V., Gitari, W.M., Ngulube, T., 2015. Kinetics and equilibrium studies for removal of fluoride from underground water using cryptocrystalline magnesite. J. Water Reuse Desal. 1, 282–292.

Mekatel, E., Amokrane, S., Aid, A., Nibou, D., Trari, M., 2015. Adsorption of methyl orange on nanoparticles of a synthetic zeolite NaA/CuO. C. R. Chim. 18, 336–344.

Mermut, A.R., 1994. Layer charge characteristics of 2:1 silicate clay minerals. In: CMS Workshop Lectures, vol. 6. The Clay Minerals Society, Boulder, CO.

Merzouk, B., Yakoubi, M., Zongo, I., Leclerc, J.P., Paternotte, G., Pontvianne, S., et al., 2011. Effect of modification of textile wastewater composition on electro-coagulation efficiency. Desalination 275, 181–186.

Mitchell, J.K., 1993. Fundamentals of Soil Behaviour, second ed. Wiley, New York, pp. 405–445.

Miyamoto, N., Kawai, R., Kuroda, K., Ogawa, M., 2000. Adsorption and aggregation of a cationic cyanine dye on layered clay minerals. Appl. Clay Sci. 16, 161–170.

Mohan, D., Singh, K.P., Singh, G., Kumar, K., 2007. Removal of dyes from wastewater using flyash, a low-cost adsorbent. Ind. Eng. Chem. Res. 41, 3688–3695.

Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, New York, NY.

Mu, B., Wang, A., 2016. Adsorption of dyes onto palygorskite and its composites: a review. J. Environ. Chem. Eng. 4, 1274–1294.

Mudzielwana, R., Gitari, W.M., Msagati, T.A.M., 2016. Characterization of smectite rich clay soils: implication for groundwater defluoridation. South Afr. J. Sci. 112 (11/12), 1–8.

Nandi, B.K., Goswami, A., Purkait, M.K., 2009. Adsorption characteristics of brilliant green dye on kaolin. J. Hazard. Mater 161, 387–395.

Ogunmodede, O.T., Ojo, A.A., Adewole, E., Adebayo, O.L., 2015. Adsorptive removal of anionic dye from aqueous solutions by mixture of Kaolin and Bentonite clay: characteristics, isotherm, kinetic and thermodynamic studies. Iran. J. Energy Environ. 6 (2), 147–153.

Oremusová, J., 2007. Manual for laboratory practice in physical chemistry for students of pharmacy. Department of Physical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, in Slovak.

Ozcan, A.S., Erdem, B., Ozcan, A., 2004. Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. J. Colloid Interface Sci. 280, 44–54.

Özcan, A.S., Özcan, A., 2004. Adsorption of acid dyes from aqueous solutions onto acid activated bentonite. J. Colloid Interface Sci. 276, 39–46.

Özcan, A.S., Erdem, B., Özcan, A., 2005. Adsorption of Acid Blue 193 from aqueous solutions onto BTMA–bentonite. Colloids Surf. A Physicochem. Eng. Asp. 266, 73–81.

Ozcan, A., Omeroglu, C., Erdogan, Y., Ozcan, A.S., 2007. Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19. J. Hazard. Mater 140, 173–179.

Pajootan, E., Arami, M., Mohammad, N., 2012. Binary system dye removal by electrocoagulation from synthetic and real colored wastewaters. J. Taiwan Inst. Chem. Eng. 43, 282–290.

Peng, X., Luan, Z., Zhang, H., 2006. Montmorillonite-Cu(II)/Fe(III) oxides magnetic material as adsorbent for removal of humic acid and its thermal regeneration. Chemosphere 63, 300–306.

Peng, L., Qin, P., Lei, M., Zeng, Q., Song, H., Yang, J., Shao, J., Liao, B., Gu, J., 2012. ModifyingFe3O4 nanoparticles with humic acid for removal of Rhodamine B in water. J. Hazard. Mater 209–210, 193–198.

Peng, Y.G., Chen, D.J., Ji, J.L., Kong, Y., Wan, H.X., Yao, C., 2013. Chitosan-modified palygorskite: preparation, characterization and reactive dye removal. Appl. Clay Sci. 74, 81–86.

Pinnavaia, T., 1983. Intercalated clay catalysts. J. Sci. 220 (4595), 365–371.

Qureshi, K., Ahmad, M.Z., Bhatti, I.A., Iqbal, M., Khan, A., 2015. Cytotoxicity reduction of wastewater treated by advanced oxidation process. Chem. Int. 1, 53–59.

Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A., 2010. Adsorption of methylene blue on low-cost adsorbents: a review. J. Hazard Mater 177 (1–3), 70–80.

Rehman, M.S.U., Munira, M., Ashfaqa, M., Rashid, N., Nazar, M.F., et al., 2013. Adsorption of Brilliant Green dye from aqueous solution onto red clay. Chem. Eng. J. 228, 54–62.

Reza-Mahdavinia, G., Aghaie, H., Sheykhloie, H., Vardini, M.T., Etemadi, H., 2013. Synthesis of CarAlg/MMt nanocomposite hydrogels and adsorption of cationic crystal violet. Carbohydr. Polym. 98, 358–365.

Robinson, T., McMullen, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour. Technol. 77, 247–255.

Roulia, M., Vassiliadis, A.A., 2008. Sorption characterization of a cationic dye retained by clays and perlite. Micropor. Mesopor. Mater. 116 (1–3), 732–740.

Sabah, E., Mart, U., Çınar, M., Çelik, M.S., 2007. Zeta potentials of sepiolite suspensions in concentrated monovalent electrolytes. Sep. Sci. Technol. 42, 2275–2288.

Safa, Y., Bhatti, H.N., 2011. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. Desalination 272, 313–322.

Saha, B., Das, S., Saikia, J., Das, G., 2011. Preferential and enhanced adsorption of different dyes on iron oxide nanoparticles: a comparative study. J. Phys. Chem. C 115, 8024–8033.

Santos, S.C.R., Boaventura, R.A.R., 2016. Adsorption of cationic and anionic azo dyes on sepiolite clay: equilibrium and kinetic studies in batch mode. J. Environ. Chem. Eng. 4, 1473–1483.

Santos, S.C.R., Oliveira, A.F.M., Boaventura, R.A.R., 2016. Bentonitic clay as adsorbent for the decolourisation of dyehouse effluents. J. Clean. Prod. 126, 667–676.

Sarkar, B., Xi, Y.F., Megharaj, M., Naidu, R., 2011. Orange II adsorption on palygorskites modified with alkyl trimethylammonium and dialkyl dimethylammonium bromide - an isothermal and kinetic study. Appl. Clay Sci. 51, 370–374.

Sarma, G.K., Gupta, S.S., Bhattacharyya, K.G., 2016. Adsorption of Crystal violet on raw and acid-treated montmorillonite, K10, in aqueous suspension. J. Environ. Manag. 171, 1–10.

Savic, I., Gajic, D., Stojiljkovic, S., Savic, I., di Gennaro, S., 2014. Modeming and optimization of methylene blue adsorption from aqueous solution using bentonite clay. Comput. Aided Chem. Eng. 33, 1417–1422.

Schacht, E.H., 2004. Polymer chemistry and hydrogel system. Phys. Conf. Ser. J. 3, 22.

Shamraiz, U., Hussain, R.A., Badshah, A., Raza, B., Sab, S., 2016. Functional metal sulfides and selenides for the removal of hazardous dyes from water. J. Photochem. Photobiol. B Biol. 159, 33–41.

Shichi, T., Takaqi, K., 2000. Clay minerals as photochemical reaction fields. J. Photochem. Photobiol. C. Photochem. Rev. 1, 113–130.

Shirsath, S.R., Patil, A.P., Patil, R., Naik, J.B., Gogate, P.R., Sonawane, S.H., 2013. Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly (acrylic acid) hydrogel loaded with kaolin clay: a comparative study. Ultrason. Sonochem. 20, 914–923.

Shirsath, S.R., Hage, A.P., Zhou, M., Sonawane, S.H., Ashokkumar, M., 2011. Ultrasound assisted preparation of nanoclay Bentonite-FeCo nanocomposites hybrid hydrogel: a potential responsive sorbent for removal of organic pollutant from water. Desalination 281, 429–437.

Shon, H., Phuntsho, S., Chaudhary, D., Vigneswaran, S., Cho, J., 2013. Nano filtration for water and wastewater treatment – a mini review. Drinking Water Eng Sci 6, 47–53.

Singh, S.A., Vemparala, B., Madras, G., 2015. Adsorption kinetics of dyes and their mixtures with Co_3O_4–ZrO_2 composites. J. Environ. Chem. Eng. 3, 2684–2696.

Spark, K.M., Wells, J.D., Johnson, B.B., 1995. Characterizing trace metal adsorption on kaolinite. Eur. J. Soil Sci. 46, 633–640.

Srinivasan, R., 2011. Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Adv. Mater. Sci. Eng., 872531

Srivastava, V., Sillanpää, M., 2016. Synthesis of malachite@ clay nanocomposite for rapid scavenging of cationic and anionic dyes from synthetic wastewater. J. Environ. Sci. http://dx.doi.org/10.1016/j.jes.2016.08.011.

Suraj, G., Iyer, C.S.P., Rugmini, S., Lalithambika, M., 1998. Adsorption of cadmium and copper by modified kaolinites. Appl. Clay Sci. 13, 293–306.

Tabak, A., Eren, E., Afsin, B., Caglar, B., 2009. Determination of adsorptive properties of a Turkish Sepiolite for removal of Reactive Blue 15 anionic dye from aqueous solutions. J. Hazard. Mater 161, 1087–1094.

Tahir, M.A., Bhatti, H.N., Iqbal, M., 2016. Solar Red and Brittle Blue direct dyes adsorption onto Eucalyptus angophoroides bark: equilibrium, kinetics and thermodynamic studies. J. Environ. Chem. Eng. 4, 2431–2439.

Tehrani-Bagha, A.R., Nickers, H., Mahmoodi, N.M., Markazi, M., Menger, F.M., 2011. The sorption of cationic dyes onto kaolin: kinetic, isotherm and thermodynamic studies. Desalination 266 (1), 274–280.

Tümsek, F., Avci, Ö., 2013. Investigation of kinetics and isotherm models for the acid orange 95 adsorption from aqueous solution onto natural minerals. J. Chem. Eng. Data 58, 551–559.

Tomar, V., Prasad, S., Kumar, D., 2014. Adsorptive removal of fluoride from aqueous media using citrus limonum (lemon) leaf. Microchem. J. 112, 97–103.

Toor, M., Jin, B., 2012. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem. Eng. J. 187, 79–88.

Uyar, G., Kaygusuz, F.H., Erim, B., 2016. Methylene blue removal by alginate–clay quasi-cryogel beads. React. Funct. Polym. 106, 1–7.

Vimonses, V., Lei, S., Jin, B., Chow, C.W.K., Saint, C., 2009. Kinetic study and equilibrium isotherm analysis of Congo red adsorption by clay materials. Chem. Eng. J. 148, 354–364.

Wang, W.B., Wang, F.F., Kang, Y.R., Wang, A.Q., 2015. Enhanced adsorptive removal of methylene blue from aqueous solution by alkali-activated palygorskite. Water Air Soil Pollut. 226, 83.

Wang, X., Huang, H., Li, G., 2014. Hydrothermal synthesis of 3D hollow porous Fe_3O_4 microspheres towards catalytic removal of organic pollutants. Nanoscale Res. Lett. 9, 1–5.

Wang, Y., Zeng, L., Ren, X., Song, H., Wang, A., 2010. Removal of Methyl Violet from aqueous solutions using poly (acrylic acid-co acrylamide)/attapulgite composite. Environ. Sci. J. 22 (1), 7.

Watanabe, T., Miki, Y., Masuda, T., Kanai, H., Hosokawa, S., Wada, K., Inoue, M., 2011. Pore structure of c-Ga_2O_3–Al_2O_3 particles prepared by spray pyrolysis. Micropor. Mesopor. Mater. 145, 131–140.

Weng, C.H., Lin, Y.T., Tzeng, T.W., 2009. Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder. J. Hazard. Mater 170, 417–424.

Worch, E., 2012. Adsorption Technology in Water Treatment: Fundamentals, Processes and Modelling. Walter de Gruyter GmbH & Co. KG, Berlin/Boston.

Xu, P., Zeng, G., Huang, D., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. Sci. Total Environ. 424, 1–10.

Xue, A.L., Zhou, S.Y., Zhao, Y.J., Lu, X.P., Han, P.F., 2010. Adsorption of reactive dyes from aqueous solution by silylated palygorskite. Appl. Clay Sci. 48, 638–640.

Xue, A.L., Zhou, S.Y., Zhao, Y.J., Lu, X.P., Han, P.F., 2011. Effective NH2-grafting on attapulgite surfaces for adsorption of reactive dyes. J. Hazard. Mater 194, 7–14.

Yan, L., Qin, L., Yu, H., Li, S., Shan, R., Du, B., 2015. Adsorption of acid dyes from aqueous solution by CTMAB modified bentonite: kinetic and isotherm modelling. J. Mol. Liq. 21, 1074–1081.

Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M., 2014. Dye and its removal from aqueous solution by adsorption: a review. Adv. Colloid Interface Sci. 209, 172–184.

Yousef, R.I., El-Eswed, B., Al-Muhtaseb, A.H., 2011. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism and thermodynamics studies. Chem. Eng. J. 171, 1143–1149.

Yu, X., Wei, C., Wu, H., 2015. Effect of molecular structure on the adsorption behavior of cationic dyes onto natural vermiculite. Sep. Purif. Technol. 156, 489–495.

Zhang, J., Cai, D.Q., Zhang, G.L., Cai, C.J., Zhang, C.L., Qiu, G.N., Zheng, K., Wu, Z.Y., 2013. Adsorption of methylene blue from aqueous solution onto multiparous palygorskite modified by ion beam bombardment: effect of contact time temperature, pH and ionic strength. Appl. Clay Sci. 83–84, 137–143.

Zhang, Y., Wang, W.B., Zhang, J.P., Liu, P., Wang, A.Q., 2015a. A comparative study about adsorption of natural palygorskite for methylene blue. Chem. Eng. J. 262, 390–398.

Zhang, Z.F., Wang, W.B., Wang, A.Q., 2015b. High-pressure homogenization associated hydrothermal process of palygorskite for enhanced adsorption of methylene blue. Appl. Surf. Sci. 329, 306–314.

Zhang, Z.H., Zhu, H.J., Zhou, C.H., Wang, H., 2016. Geopolymer from kaolin in China: an overview. Appl. Clay Sci. 119, 31–41.

Zhao, Y., Abdullayev, E., Vasiliev, A., Lvov, Y., 2013. Halloysite nanotubule clay for efficient water purification. J. Colloid Interface Sci. 406, 121–129.

Zhou, K., Zhang, Q., Wang, B., Liu, J., Wen, P., Gui, Z., Hu, Y., 2014. The integrated utilization of typical clays in removal of organic dyes and polymer nanocomposites. J. Clean. Prod. 81, 281–289.

Zhou, Z., Gunter, W.D., 1992. The nature of the surface charge of kaolinite. Clay Miner. 40, 365–368.

Zhu, L.Z., Chen, B.L., 2000. Sorption behavior of p-nitrophenol on the interface between anion–cationic organobentonite and water. Environ. Sci. Technol. 34, 2997–3002.

Zollinger, H., 1987. “Fluorescent brighteners” in color chemistry. VCH, Weinheim, pp. 203–213.

Zulfikar, M.A., 2013. Materials, Effect of temperature on adsorption of humic acid from peat water onto pyrophyllite. Int. J. Chem. Environ. Biol. Sci. 1, 88–91.