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Synthesis, characterization and performance evaluation of groundwater defluoridation capacity of smectite rich clay soils and Mn-modified bentonite clay composites

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ABSTRACT

Several studies revealed that some of the boreholes within South Africa have F^- concentration above 1.5 mg/L. This study evaluates the use of black smectite rich clay soils from Mukondeni, Mn^{2+} modified bentonite, MnO_2 coated Na-bentonite clay and MnO_2 coated Na-bentonite/smectite rich clay soils composite for defluoridation of groundwater. Mn^{2+} modified bentonite was prepared via ion exchange mechanism and MnO_2 coated Na-bentonite was synthesised by prior activating bentonite using NaOH followed by *in-situ* reduction of $KMnO_4$. The composite was prepared by mixing MnO_2 coated Na-bentonite and smectite rich clay soils at varying ratios followed by moulding into pellets manually. Physicochemical and mineralogical characterization was carried out using XRD, XRF, SEM, BET, FTIR, CEC, and pH_{pzc} techniques. Batch experiments were conducted to evaluate and optimize various operational parameters such as contact time, adsorbent dose, pH and initial adsorbate concentration.

Elemental composition revealed that smectite rich clay soils mainly consist of SiO_2 and Al_2O_3 as major elements; minor components include CaO, Na_2O, MgO and traces of K_2O TiO_2 and MnO. Mineralogical analysis revealed that the clay soils consist of montmorillonite, quartz, albite and anthophyllite. It was observed that 0.8 g/100 mL of smectite rich clay soils removed up to 91.89% from the initial F^- concentration of 3 mg/L at pH of 2 and contact time of 30 min. The experimental data fitted well to Langmuir adsorption isotherm than Freundlich isotherm and followed pseudo second order reaction kinetics. Smectite rich clay soils showed 51.72% F^- removal from field groundwater with 5.4 mg/L initial F^-. Sorption of fluoride occurred via ligand exchange mechanism.

Modification of bentonite clay with Mn^{2+} increased MnO content from 0.09% in raw bentonite to 0.29% in Mn^{2+} modified bentonite clay and further decreased content of Na_2O, CaO and MgO as well as K_2O. Modification of bentonite clay with Mn^{2+} ion lead to the formation of new bonds such as Mn-O, Mn-OH and Mn-H_2O in the bentonite clay surface, this was confirmed using FTIR. Optimum operation conditions for adsorption of fluoride were established to be 30 min contact time 1.0 g/100 mL adsorbent dosage, 3 mg/L adsorbate concentration and pH of 2. Maximum percentage F^- removal of 84.0% was achieved at optimized conditions. The adsorption isotherm data fitted well to Langmuir model showing that the adsorbent is monolayer. Kinetic modelling showed that the data fitted well to pseudo second order than to the pseudo first order indicating that the rate limiting factor is chemisorption.

Coating Na-bentonite with MnO_2 lead to the formation of new minerals such as cryptomelane (KMn_8O_{16}) jacobsite $(Mn_6Fe_4)O_4$ and pyrolusite (MnO_2) which are both the oxides of manganese. Coating increased the percentage composition of Mn in the Na-bentonite and this diluted the percentage of other oxides such as SiO_2, Al_2O_3, MgO and Fe_2O_3. Optimum conditions for fluoride removal were found to be, 30 min contact time at 250 rpm, 1.5 g/100 mL adsorbent dosage, 5 mg/L adsorbate concentration, and pH of 8. Maximum F^- removal of ≈94.66% was achieved under optimum conditions. The adsorption data fitted well to Langmuir adsorption isotherm while the kinetics data fitted well to pseudo second order of reaction kinetics. Intra-

particle diffusion model of Weber-Morris indicated that the removal of fluoride by MnO_2 coated Na-bentonite is a highly complex process, involving boundary layer diffusion and intra-particle diffusion as well as equilibrium adsorption. Sorption of fluoride occurred via ligands exchange mechanism at pH below 3 and at pH above 3 it occurred via ion exchange mechanism.

The ratio of MnO_2 coated Na-bentonite clay/smectite rich clay soils for fabricating the composite was established to be 1:3. The optimum calcination temperature was found to be 550 °C. Mineralogical characterisation of the clay composite showed the presence of quartz, albite, cryptomelane and microcline as the main minerals of the calcined pellets. XRF analysis showed that SiO_2, Al_2O_3, MnO and Fe_2O_3 are the major oxides of the clay composite. Pellets prepared under the established optimum conditions removed ≈63.3% F^- from an initial F^- concentration of 10 mg/L.

Based on the findings of the study smectite rich clay soils, Mn^{2+} bentonite and MnO_2 coated Na-bentonite and the fabricated pellets can be used for defluoridation of groundwater in rural areas and the study further recommended the modification of smectite rich clay to improve its fluoride binding capacity. MnO_2 coated Na-bentonite showed higher adsorption capacity at wider range of pH however the stability test showed that the material is not stable since it released secondary contaminants into the treated water, therefore it is recommended that future work should focus on improving the stability of the mater. The study also recommend that future study should evaluate the use of MnO_2 coated Na-bentonite/smectite rich clay soils composite pellets for fluoride removal in a dynamic flow set-up.