

# PHYSICAL CHEMISTRY OF WATER TREATMENT PROCESSES

## Removal of Fe and Mn from Polluted Water Sources in Lesotho using Modified Clays

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**Abstract** - This paper reports the use of unfunctionalized and phenylalanine functionalized clays as an alternative cost effective, environmental friendly and efficient sorbent for the removal of Mn and Fe from polluted drinking water sources in Lesotho. Mn and Fe were found to be the most prevalent metal pollutants in rivers supplying three drinking water treatment plants situated in Maseru, Roma and Quthing. The Mn and Fe metals were adsorbed on two different clays (clay A – a black clay and clay B – a yellow clay) collected from Ha-Teko in Maseru (clay A) and Phoqoane in Mafeteng district (clay B) in Lesotho. As a common assessment for adsorption materials, comprehensive batch test studies were performed to assess the effect of pH, stirring time, initial concentration and kinetic studies of the adsorption of these metals. The adsorption of the metals was greater at higher pH and equilibrium was reached at pH 8.0 after 30 min of stirring. The phenylalanine functionalized clays displayed improved adsorption efficiency of up to 100 % (Fe adsorption using modified clay A in 30 min) while the unfunctionalized clays gave relatively low adsorption of up to 70 % (Fe and Mn adsorption using modified clay A). This was observed on real and simulated water samples. The findings of this work suggest that the clays, which are present in abundance in Lesotho, can be effectively used for the removal of Fe and Mn from drinking water sources in Lesotho.

**Key words:** Adsorption · clay · phenylalanine · water purification · manganese · iron

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## INTRODUCTION

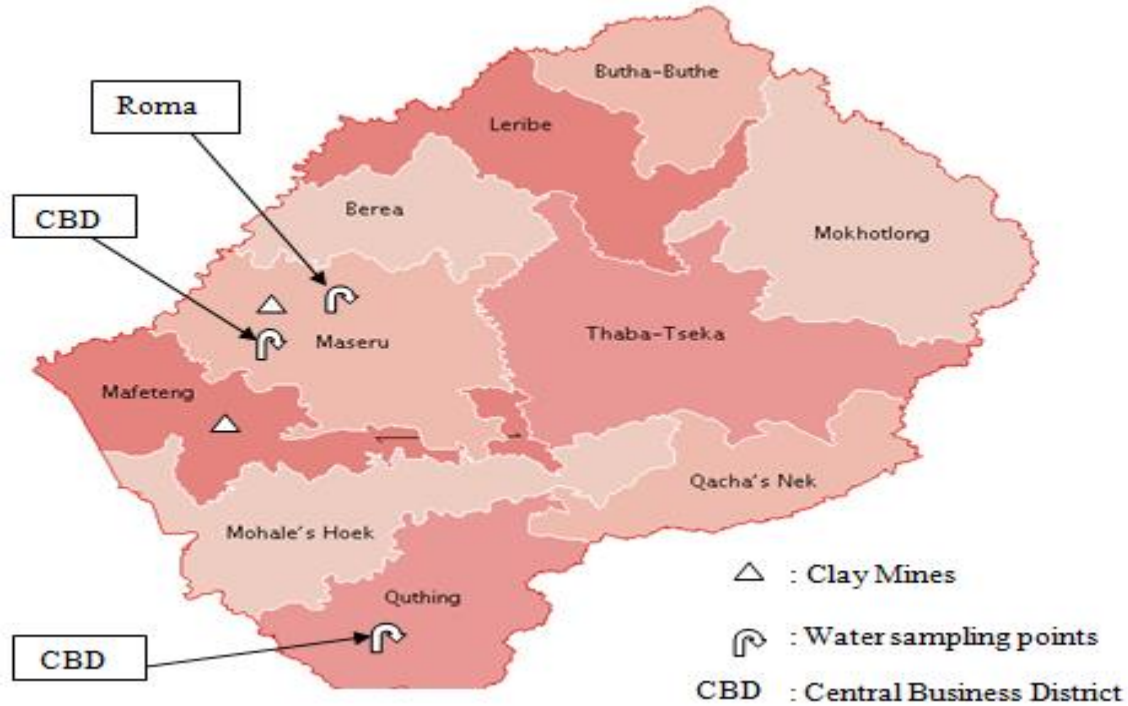
Sewage discharges, urban runoffs, agricultural wastes, industrial effluents and open pit latrines located nearby water sources are known to introduce a lot of harmful pollutants in water sources [1, 2]. This presents a real threat as heavy metals may also be entrained to water treatment systems. The presence of high concentrations of Fe and Mn ions in water sources in Lesotho is a growing concern. These metals can cause death when present at high concentrations due to their toxicity.  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions that are not removed prior to distribution of treated water to the communities are oxidized in the presence of oxygen and chlorine to form a dark-brown colour which recedes the aesthetic appearance of potable water [3]. Assimilation of high concentrations of Mn (higher than  $0.4 \text{ mgL}^{-1}$  in potable water) has been reported to cause brain malfunctioning and results in neurotic disorder, while concentrations of Fe above  $3 \text{ mgL}^{-1}$  can cause diseases like diabetes, cardiopathy and kidney failure [4, 5].

The most commonly used drinking water treatment processes include coagulation, flocculation, filtration, ion exchange, membrane filtration and adsorption. These processes have been reported to have challenges related to the removal of high concentrations of heavy metals and emerging contaminants in the water [6]. Cost effective and environmentally friendly water purification technologies continue to be sought and developed by many researchers worldwide [7]. Water purification by adsorption has been extensively explored due to its high efficiency, re-usability, availability, low cost, low toxicity and ease of handling [8]. In particular, clay materials as adsorbents have attracted much interest due to their high specific surface area and high adsorption capacity [9]. Lesotho is characterized by clay minerals found in abundance at both the lower and upper catchment of the country [10]. Others have shown that these clay minerals are rich in zeolites, silicates and iron-titanium oxide and these minerals possess adsorption capacities that can be used for removal of heavy metals in water [11]. In this work, the adsorption of Fe and Mn using locally available clay minerals was investigated.

69 EXPERIMENTAL

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71 *Sample Collection*

72 The clay samples were collected from brick producing companies in Lesotho and purified  
73 before adsorption studies. The water samples were collected from Roma, Maseru central, and  
74 Quthing water treatment plant. Water samples were preserved by adding 0.2 M HNO<sub>3</sub> (1 mL) to  
75 each water sample before storage. The sampling locations are shown in the Lesotho map given in  
76 Fig. 1. The study area was chosen due to production of water with poor quality.



**Fig. 1.** Water sampling points and clay collection sites of the study.

*Sample Preparation*

81 The clay samples were crushed and sieved using 20 µm pore sized sieves. 20 g of each  
82 clay sample was added to a separate beaker containing 50 mL of de-ionized water and stirred for  
83 30 min. The pH of the resulting mixture was measured using a pH meter. All mixtures were  
84 acidified with 3 M H<sub>2</sub>SO<sub>4</sub>. The strong acid was chosen to remove all the metal ions which are  
85 naturally adsorbed in the cavities of the clay, thereby conditioning them for better adsorption.  
86 The acidified clay solutions were stirred for 30 min and allowed to settle. The supernatants were  
87 decanted and the clays were washed several times with acidified distilled water until the

88 supernatant liquid gave a negative test for Fe, Mn and other metals. This was done to remove the  
89 metals which are naturally bound on the clays in order to increase their adsorption capacity. The  
90 pH of the clays was adjusted to their natural pH using CH<sub>3</sub>COOH/CH<sub>3</sub>COONa buffer solution  
91 with pH 6.5 as well as 1 % HNO<sub>3</sub> and 1 % NaOH solutions. The clays were filtered and dried in  
92 an oven at 105 °C. They were then labeled as clay A = black clay and clay B = yellow clay.

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#### 94 *Modification of Clays*

95 A procedure reported by Ray (2006) was followed to modify the clays. Typically,  
96 distilled water (25 mL), phenylalanine (Phe) (2 g), H<sub>2</sub>SO<sub>4</sub> (4 mL) were added into the beaker and  
97 stirred to form a homogeneous solution. Phenylalanine was found to be the best solvent to use  
98 for modification of the clays since it has binding sites that can be used for adsorption of heavy  
99 metals. The other reason to use it was that it is not toxic and does not leach into solution [12].  
100 The mixture was stirred for 15 min and the reaction vessel was allowed to cool to room  
101 temperature. Thereafter, HNO<sub>3</sub> (2 mL) was added drop wise to the mixture with constant  
102 stirring. The resulting mixture was cooled in an ice bath to 0 °C and 10 g of clay A or B was  
103 added. The mixture was further stirred for 30 min at 40 °C and the resulting modified clay was  
104 filtered and dried in an oven at 105 °C for 48 h.

105

#### 106 *Characterization of Clays*

107 The chemical composition of the clays was ascertained using X-ray fluorescence with a  
108 Axios<sup>mAX</sup> wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The particle size  
109 of the clays was analyzed using a hydrometer. Sodium hexametaphosphate Na<sub>6</sub>(PO<sub>3</sub>)<sub>6</sub> (5%) was  
110 used as the dispersing solution. The blank of the dispersing solution was prepared by diluting 5  
111 % Na<sub>6</sub>(PO<sub>3</sub>)<sub>6</sub> to a desired dilution. 30 g of clay and 100 mL of 5 % Na<sub>6</sub>(PO<sub>3</sub>)<sub>6</sub> were added into a  
112 beaker. This mixture was stirred for 2 min and allowed to settle. The suspension was transferred  
113 to a measuring cylinder. The hydrometer readings were taken at 40 sec and 412 min. The amount  
114 of clay, silt and sand were calculated using the following equations.

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$$116 \quad \% \text{ clay} = \frac{\text{corrected hydrometer reading at 412 min}}{\text{weight of sample}} \times 100 \% \quad (1)$$

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$$\% \text{ silt} = \frac{\text{corrected hydrometer reading at 40 sec}}{\text{weight of sample}} \times 100 \% - \% \text{ clay} \quad (2)$$

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$$\% \text{ sand} = 100 \% - (\% \text{ clay} + \% \text{ silt}) \quad (3)$$

121

122 The functional groups of the clays were analyzed using Perkin Elmer Spectrum 100 FTIR  
123 spectrometer. X-ray diffraction (XRD) was conducted on dry powdered samples using a Rigaku  
124 Ultimate IV diffractometer. The XRD patterns were analyzed qualitatively using “PDXL”  
125 software, provided with JCPDS-PDF2<sup>1</sup> database.

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127 *Adsorption of Fe and Mn from Simulated Water Samples*

128 A known amount of purified clay was added to a 500 mL beaker. To this, 50 ml of the  
129 aqueous solutions of known concentrations of MnO<sub>2</sub> or FeCl<sub>2</sub> was added. The pH of the solutions  
130 adjusted using 8 M NaOH and 2 M HCl and then stirred for 20 min with magnetic stirrer. The  
131 solutions were then filtered under vacuum. Fe and Mn concentrations were determined from the  
132 feed and filtrate using the UV-Vis Spectrophotometer (DR/2000).

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134 *Determination of the Effect of pH on the Adsorption of Fe and Mn Using Clays A and B*

135 A 25 mL solution of FeCl<sub>2</sub> (5 ppm) and clay A were added to five beakers. The pH of the  
136 mixtures was adjusted to 3, 5, 8, 10 and 12. Each solution was stirred for 30 min and then filtered  
137 under vacuum pressure. The concentration of Fe was measured from the feed and filtrate. The  
138 same procedure was conducted for adsorption of Mn using MnO<sub>2</sub> (5ppm) solution. Clay B was  
139 also tested for adsorption of Fe and Mn using the same procedure. Adsorption efficiency of the  
140 clay was calculated using Eq. (4).

141

142 
$$\text{Adsorption efficiency (AE)} = \frac{\text{mass of adsorbate adsorbed}}{\text{initial mass of adsorbate}} \times 100\% \quad (4)$$

143

144 where:

145 
$$\text{mass of adsorbate adsorbed} = \text{initial mass (adsorbate)} - \text{final mass (adsorbate)} \quad (5)$$

146 
$$\text{initial mass (m}_i\text{)} = \text{initial concentration (adsorbate)} \times \text{volume used} \quad (6)$$

147 final mass ( $m_f$ ) = final concentration x volume used (7)

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149 Mass of analyte per mass of clay (m/m) =  $\frac{\text{mass of adsorbate}}{\text{mass of adsorbent}}$  (8)

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#### 152 *Effect of Stirring Time on Adsorption Fe and Mn Using Clays A and B*

153 A 25 mL solution of FeCl<sub>2</sub> (5 ppm) and clay A were added to six beakers. The pH of  
154 these mixtures was adjusted to pH 8 (using the buffer solution of pH 8, NaOH and HNO<sub>3</sub>) since  
155 it was found to be the average pH for optimal adsorption. The solutions were then stirred for 5  
156 min (solution in beaker 1), 10 (solution in beaker 2), 15 min (solution in beaker 3), 20 min  
157 (solution in beaker 4), 25 min (solution in beaker 5) and 30 min (solution in beaker 6) and  
158 filtered under vacuum. The concentration of Fe was measured from the feed and filtrate using a  
159 UV-Vis spectrophotometer. The same procedure was conducted for adsorption of Mn using  
160 MnO<sub>2</sub> (5 ppm) solution. The similar experiment was conducted using clay B for adsorption of Fe  
161 and Mn. The adsorption efficiencies were then calculated.

162

#### 163 *Effect of Initial Concentration on the Adsorption of Fe and Mn Using Clays A and B*

164 Clay A, distilled water and varying concentrations of Fe solutions (5 M, 10 M, 15 M, 20  
165 M, 25 M, 30 M) were added to six beakers. The pH of these mixtures was adjusted to pH 8 and  
166 all the solutions were stirred for 30 min and filtered under vacuum. The concentration of Fe was  
167 determined from the feed and filtrate using a UV-Vis spectrophotometer. The same procedure  
168 was conducted for adsorption of Mn using MnO<sub>2</sub> (5 M) solution as well as the adsorption on clay  
169 B for both metals. Adsorption efficiencies were then calculated.

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#### 171 *Determination of the Adsorbent Holding Capacity*

172 Clay A and Fe solution were added to a beaker. The pH of the solution was adjusted to  
173 pH 8. The mixture was stirred for 30 min and filtered under vacuum. The Fe concentration was  
174 measured from the feed and filtrate. The mass of adsorbate (Fe) adsorbed per mass of the  
175 adsorbent (clay) was calculated using Eq. (8). The same procedure was conducted for adsorption  
176 of Mn using MnO<sub>2</sub> (5 M) solution. The similar experiment was conducted using clay B on  
177 adsorption of both metals.

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*Adsorption of Fe and Mn from Real Polluted Samples*

The adsorption efficiencies of the modified clays were done on samples collected from three different locations (Fig. 1.). The sampling sites were selected due to high concentration of Fe and Mn detected in their water samples. Adsorption was done at pH 8 with stirring time of 30 min.

RESULTS AND DISCUSSION

*Characterization of Clays*

*X-Ray Fluorescence Analyses*

The chemical composition of the clays was determined using a wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. All the clays were found to have a high content of silica and a moderate content of alumina, which are known to be active sites for the adsorption of metals (Table 1). Other metal oxides were found at trace levels. The high chemical composition of silica and alumina explains the ability of these clays to remove high concentrations of Fe and Mn metals contaminants due to the presence of silanol (Si-O) and aluminol (Al-O) groups which are capable of forming inner sphere complexes with the metals at particle edges of the clay [13]. MnO is the chemical compound responsible for the appearance (colour) of black clay while V<sub>2</sub>O<sub>5</sub> is responsible for the appearance of yellow clay.

209 Table 1: The chemical composition of minerals in the clays.

| Mineral                        | Black clay, A (%) | Yellow clay, B (%) |
|--------------------------------|-------------------|--------------------|
| SiO <sub>2</sub>               | 71.8              | 71.8               |
| Al <sub>2</sub> O <sub>3</sub> | 16.4              | 14.5               |
| Na <sub>2</sub> O              | 0.10              | 0.10               |
| K <sub>2</sub> O               | 2.96              | 2.45               |
| MgO                            | 0.80              | 0.70               |
| MnO                            | 1.10              | <0.01              |
| Fe <sub>2</sub> O <sub>3</sub> | 1.42              | 4.56               |
| CaO                            | 0.22              | 0.23               |
| TiO <sub>2</sub>               | 1.05              | 0.97               |
| P <sub>2</sub> O <sub>5</sub>  | 0.03              | 0.01               |
| Cr <sub>2</sub> O <sub>3</sub> | <0.01             | <0.01              |
| V <sub>2</sub> O <sub>5</sub>  | 0.01              | 0.11               |
| SO <sub>3</sub>                | <0.01             | <0.01              |
| Cl                             | <0.01             | <0.01              |

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*Particle Size Determination*

212 The particle sizes of the clays are recorded in Table 2. The composition of the clays was  
 213 found to be 15.8% for black clay and 15.3% for yellow clay and the rest was silt and sand. The  
 214 silt and sand components play an important role in water filtration as they increase the porosity;  
 215 hence reduce energy needed for water filtration [14, 15]. It must be noted however that the  
 216 materials were classified as clays because of the physical properties they exhibited when mixed  
 217 with water.

218 Table 2: The particle size and the other components of clays.

| Composition      | Black clay, A (%) | Yellow clay, B (%) |
|------------------|-------------------|--------------------|
| clay (< 2 μm)    | 15.8              | 15.3               |
| silt (2 < 60 μm) | 54.4              | 52.3               |
| sand (> 60 μm)   | 29.8              | 32.3               |

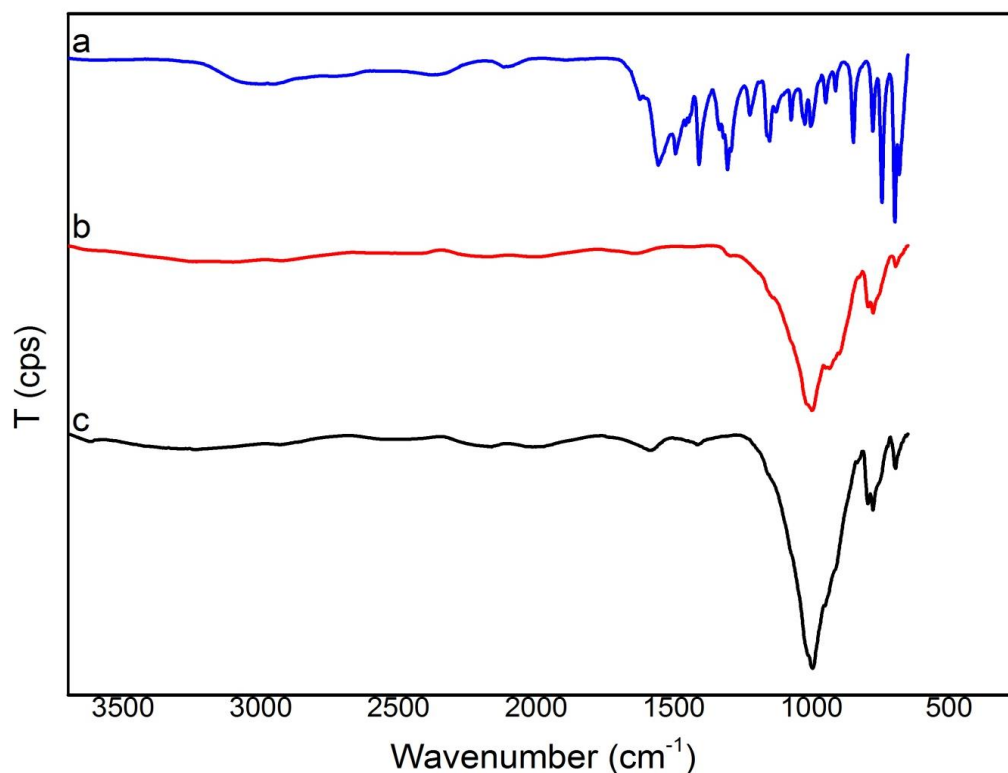
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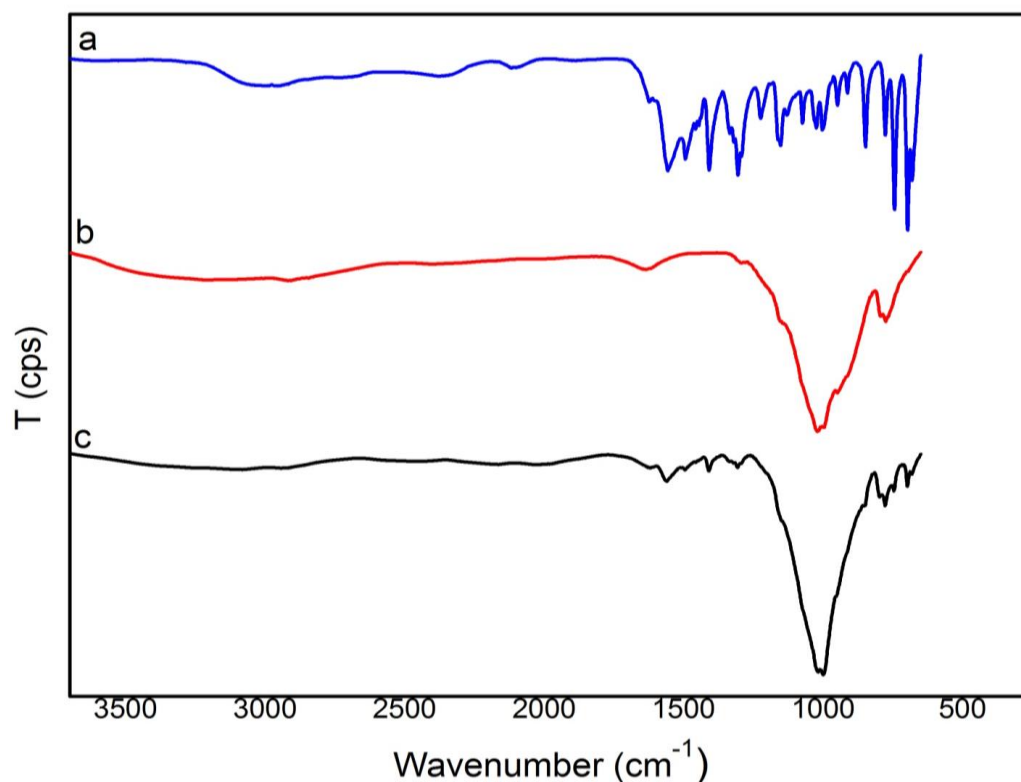
### FT-IR Analysis of the Clays

221 The FT-IR analysis of the clays was conducted to confirm their functionalization using  
222 phenylalanine (Phe) (Fig. 2 and Fig. 3). From Fig. 2 (a), the broad peak at  $3006\text{ cm}^{-1}$  is assigned  
223 to a carboxylic O-H stretches present in phenylalanine. The characteristic vibration bands of  
224 phenylalanine can also be observed at  $1622\text{ cm}^{-1}$  (C=O),  $1073\text{ cm}^{-1}$  (C-N),  $3512\text{ cm}^{-1}$  (N-H),  
225  $1128\text{ cm}^{-1}$  (C-O) stretches. The characteristic absorption bands of black clay were observed at  
226  $998\text{ cm}^{-1}$ ,  $796\text{ cm}^{-1}$ ,  $694\text{ cm}^{-1}$ ,  $3100\text{ cm}^{-1}$  belonging to Si-O, Mg-Al-OH, Al-O and O-H  
227 vibrations respectively (Fig. 2 (b)). The characteristic absorption bands of yellow clay were  
228 observed at  $794\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$  and  $3216\text{ cm}^{-1}$  belonging to Si-O, Mg-Al-OH and O-H stretches  
229 respectively (Fig. 3. (b)). The vibration bands at  $998\text{ cm}^{-1}$  (Si-O) and  $694\text{ cm}^{-1}$  (Al-O ) on black  
230 clay and  $1017\text{ cm}^{-1}$  (Si-O) on yellow clay confirm the presence of chelating groups (Al-O<sup>-</sup> and  
231 Si-O<sup>-</sup>) on modified clays. However, a shift of the C-O vibration to  $1415\text{ cm}^{-1}$  on the black clay  
232 and  $1206\text{ cm}^{-1}$  on the yellow clay confirmed the addition of Si-O and Al-O to the electrophilic  
233 carbon of the carboxylic group on phenylalanine (Fig. 2 (c)). The FTIR spectra of pure and  
234 functionalized yellow clay are presented in Fig. 3.



235

236 **Fig. 2.** FT-IR spectra of (a) Phe, (b) unfunctionalized black clay and (c) Phe-f-black clay.



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239 **Fig. 3.** FT-IR spectra of (a) Phe, (b) unfunctionalized yellow clay and (c) Phe-f-yellow clay.

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#### *XRD Analysis of the Clays*

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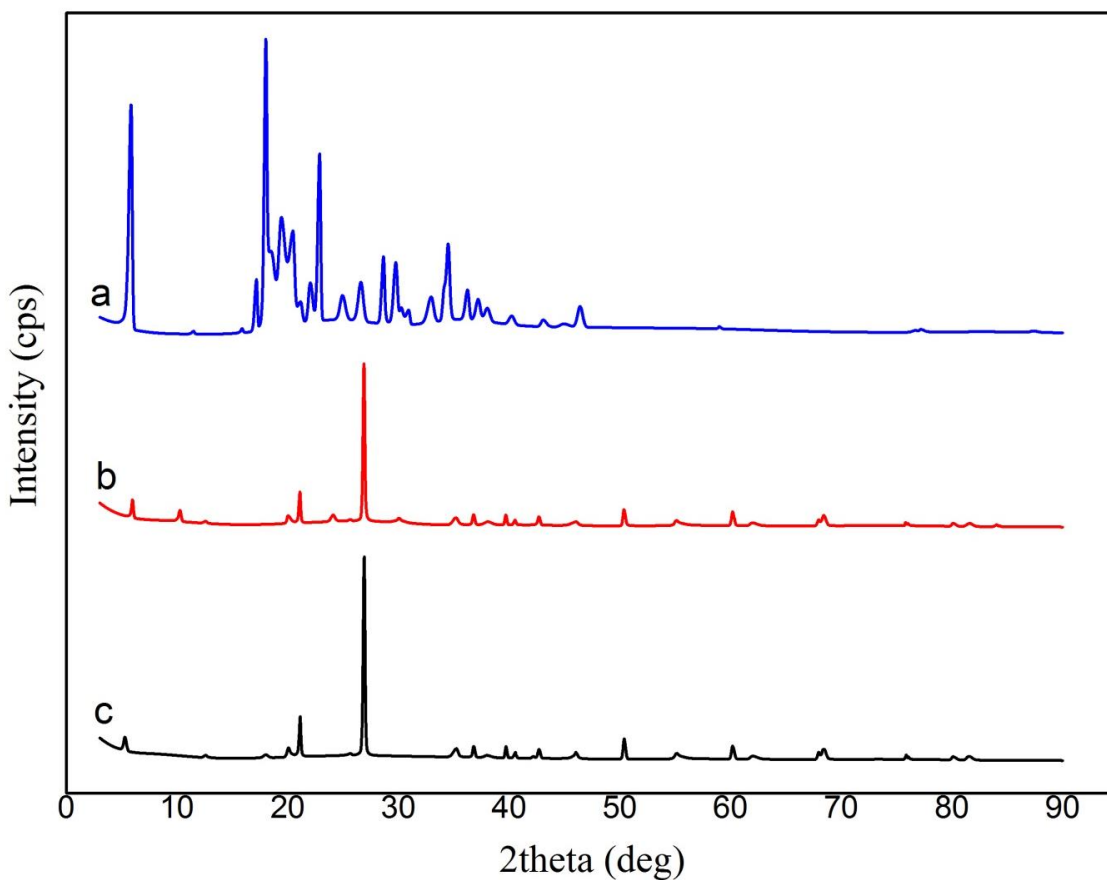
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The XRD patterns of unfunctionalized and phenylalanine functionalized black and yellow clays are shown in Figs 4 and 5. The diffraction patterns show that the crystalline nature of the silicate and aluminate in the clays was not affected by the modification with phenylalanine on both clays. This was confirmed by the peaks at  $2\theta = 26.178^\circ$  and  $36.740^\circ$  that were assigned to  $\text{SiO}_2$  and  $\text{AlO}_2$  on the black clay (Fig. 4) and  $2\theta = 26.681^\circ$  and  $36.791^\circ$  assigned  $\text{SiO}_2$  and  $\text{AlO}_2$  on the yellow clay (Fig. 5). Both clays were found to have high content of silica (60-80%) at a d-spacing of 152 nm. The black clays were found to be composed of illite (3.8%), muscovite (28%), kaolinite (7.8%), and montmorillonite (1.6%) at d-spacings of 12 nm, 5 nm, 1 nm, and 12 nm respectively (Table 3). The yellow clay was found to consist of illite (13.1%), muscovite (0.8%), kaolinite (5.7%), montmorillonite (0.03%) and bentonite (0.9%) at d-spacings of 12 nm, 5 nm, 1 nm, 12 nm and 12 nm respectively (Table 2). The XRD results thus confirmed the

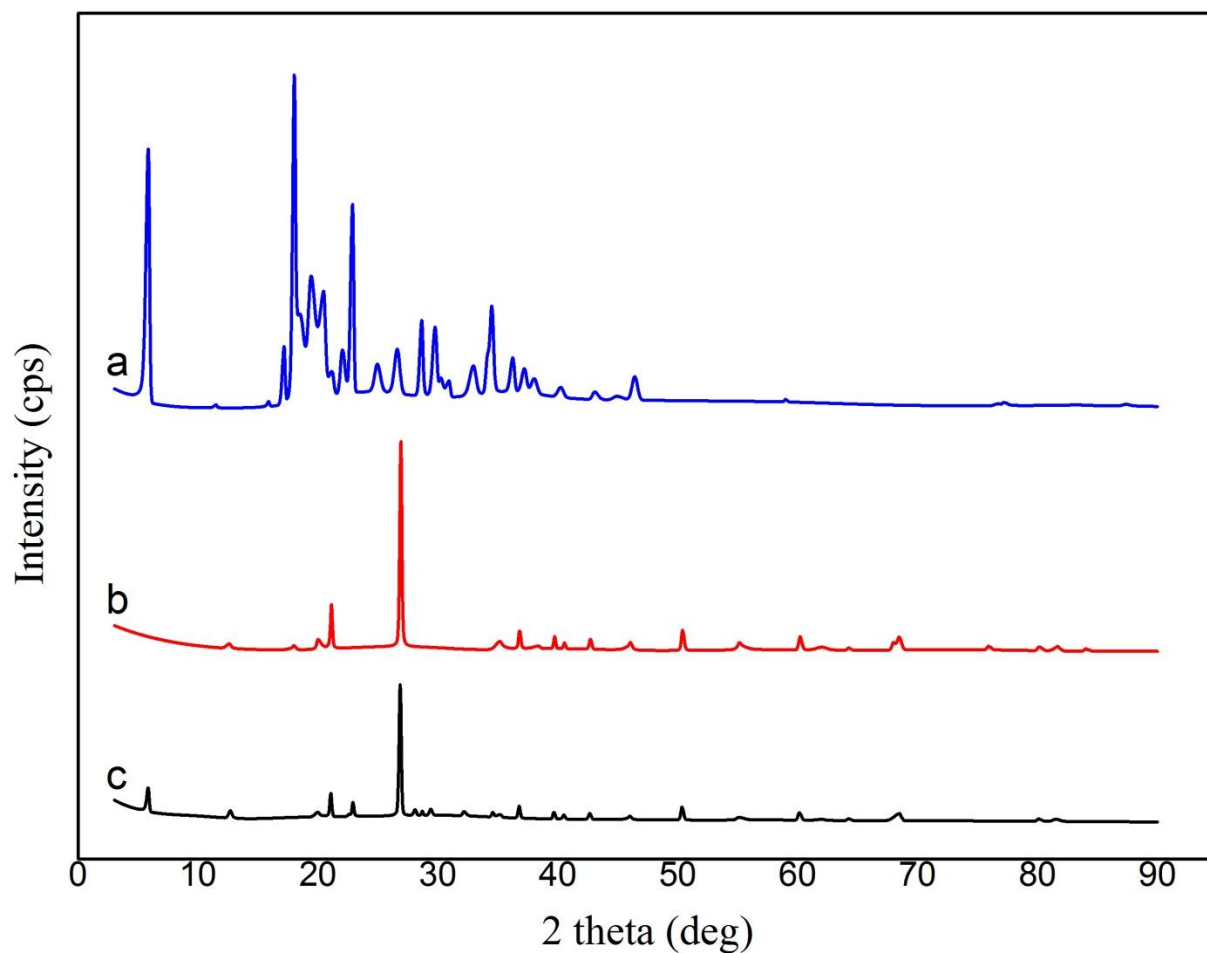
253 chemical composition and functional groups of both groups obtained from XRF and FT-IR  
254 respectively.

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256

257 **Fig. 4.** XRD patterns of (a) Phe, (b) unfunctionalized black clay and (c) Phe-f-black clay.



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 259 **Fig. 5.** XRD patterns of (a) Phe, (b) unfunctionalized yellow clay and (c) Phe-f-yellow clay.  
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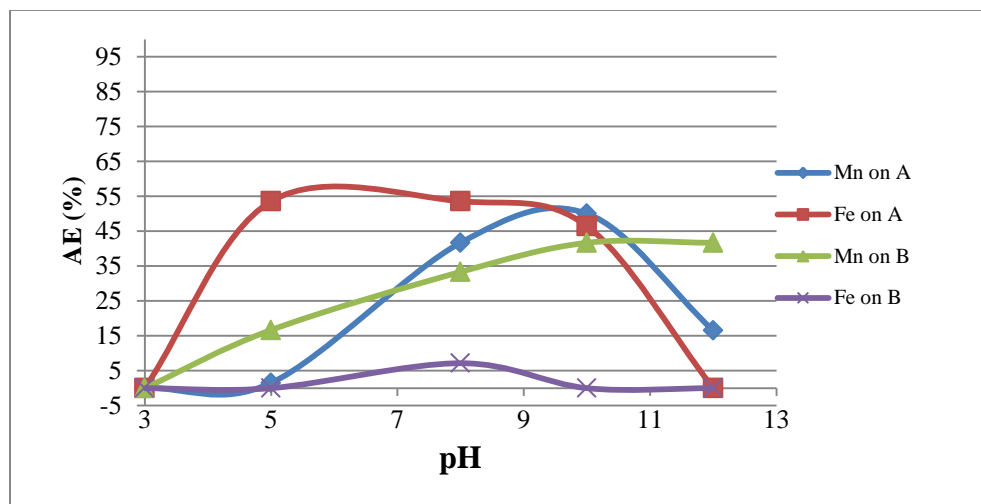
261 Table 3: Clay phases, their d-spacing and quantitative analysis.

| Phase name      | Formula  | Content (%) |             | Space groups |             |
|-----------------|--|-------------|-------------|--------------|-------------|
|                 |  | Black Clay  | Yellow Clay | Black Clay   | Yellow Clay |
| quartz          | SiO <sub>2</sub>   | 58.8        | 79.4        | 152          | 125         |
| Illite          | K <sub>0.7</sub> Al <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>  | 3.8         | 13.1        | 12           | 12          |
| Muscovite       | K Al( Mg <sub>0.2</sub> Al <sub>0.8</sub> )(Al <sub>0.42</sub> Si <sub>3.58</sub> )O <sub>10</sub> (OH) <sub>2</sub>   | 28.0        | 0.8         | 5            | 5           |
| Kaolinite       | Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>   | 7.8         | 5.7         | 1            | 1           |
| Montmorillonite | Li <sub>0.62</sub> (Al <sub>3</sub> Fe <sub>0.45</sub> Mg <sub>0.54</sub> )((Si <sub>8</sub> Al <sub>0.2</sub> )O <sub>20</sub> (OH) <sub>4</sub> )                                      | 1.6         | 0.03        | 12           | 12          |
| Bentonite       | (Ca <sub>0.2</sub> Na <sub>0.2</sub> K <sub>0.3</sub> )(Al <sub>1.6</sub> Fe <sub>0.06</sub> Mg <sub>0.3</sub> )(Al <sub>0.3</sub> Si <sub>3.7</sub> O <sub>10</sub> (OH) <sub>2</sub> ) | 0           | 0.9         | 1            | 12          |

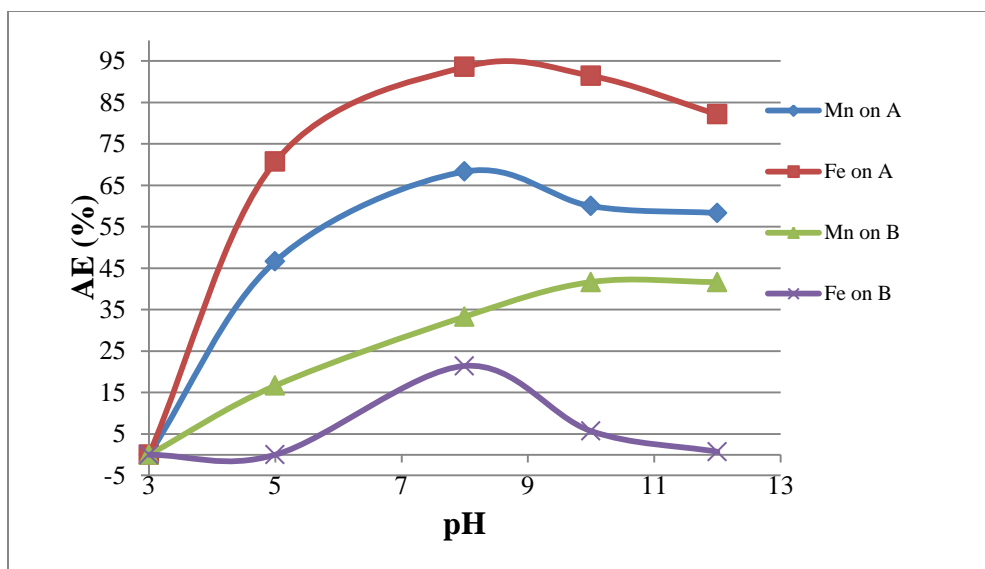
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*The Effect of pH on the Adsorption Capacities of Clay A and B*

The pH of the solution containing the metal to be adsorbed is one of the most important factors that determine the efficiency of the adsorbent. This is because pH has the potential to interact with the electronic properties of the active sites of the adsorbent and can make it less effective as an adsorbent. The effect of pH on the adsorption of Mn and Fe ions on the two different unmodified and modified black and yellow clays was studied and the results are shown in Fig. 6 and Fig. 7.



**Fig. 6.** Effect of pH on the adsorption of Fe and Mn using unmodified clay A and B.



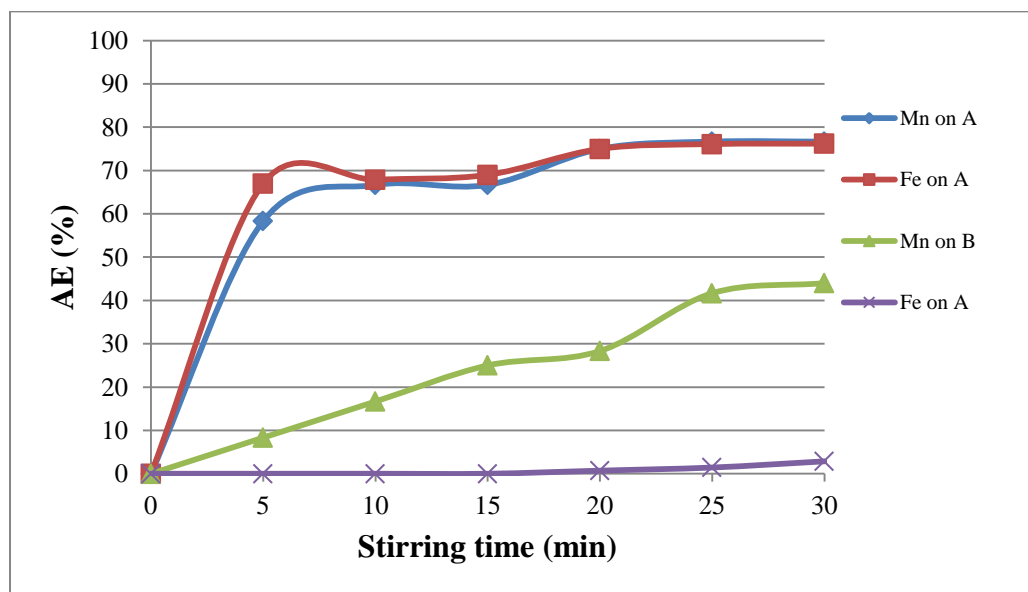
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279 **Fig. 7.** Effect of pH on the adsorption of Fe and Mn using modified clay A and B.

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281 The adsorption efficiencies of clays were found to increase with an increase in pH to  
282 neutral and slightly basic pH. Further increase in pH led to a decrease in adsorption. At lower  
283 pH, functional adsorption groups dissociate and hydronium ions compete with the metal ions at  
284 the active surface area of the clay. As the pH increases, the hydronium ion concentration  
285 decreases and nucleophilicity of the centers for adsorption of metals increases. At higher pH  
286 (*i.e.* pH > 8), there is formation of metal hydroxides which reduce the adsorption of heavy  
287 metals, thereby decreasing the adsorption efficiency of clay. Adsorption of Fe was greater than  
288 that of Mn on both modified and unmodified clay A (Fig. 6 and Fig. 7). As pH was increased and  
289 neutralization occurred, both Fe and Mn formed aqua complexes and water exchange rate of Mn  
290 was greater than that of Fe which reduced adsorption of Mn ions. A study conducted by Kamel et  
291 al. (2004) reported a greater affinity of Fe ion adsorption on kaolinite clay than that of Mn ion  
292 [16]. However, Fe adsorption was very poor on clay B probably due to lack of ion exchange and  
293 poor mass transfer from the bulk solution to the active sites of adsorption since diffusion  
294 coefficient of Fe is smaller than that of Mn on adsorption in most adsorption [17].

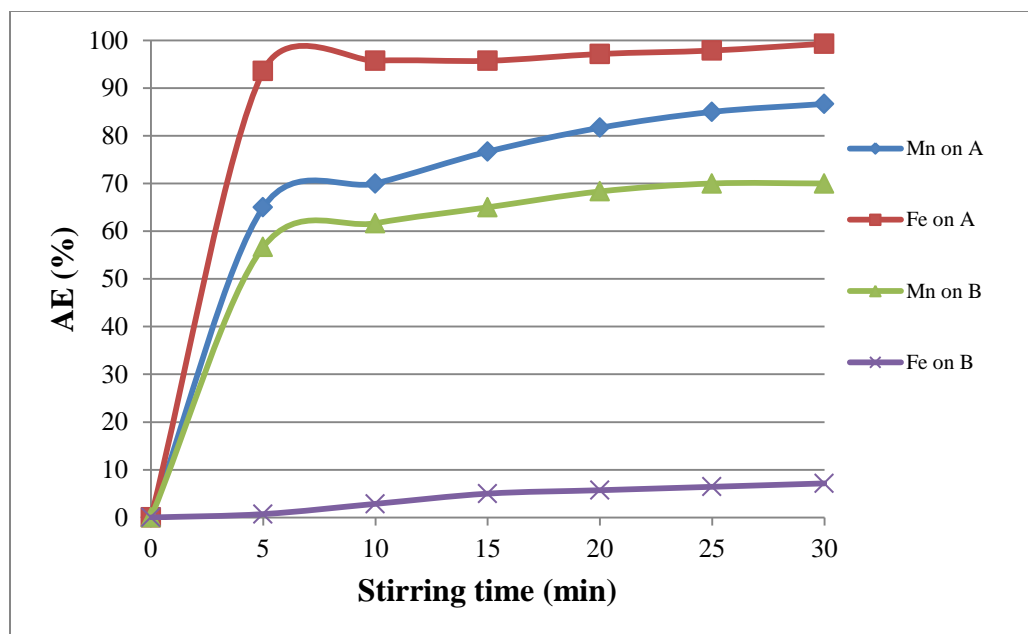
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296 *Effect of Stirring on the Adsorption Kinetics for Clays A and B*

297 The effect of stirring time of Fe and Mn on the adsorbents was also studied. The  
298 adsorption efficiencies of both modified and unmodified clays increased with increase in stirring  
299 time (Fig. 8 and Fig. 9). The adsorption of the metals increased sharply in the first 5 min as there

300 were many vacant sites available for adsorption. Further increase in contact time resulted to a  
301 slower adsorption rate because the number of active surface sites had decreased. An equilibrium  
302 (where no more adsorption) occurred at 20-30 min of stirring time for both clays. The adsorption  
303 of Fe and Mn was found to be higher on the modified clays than that of unmodified clays.  
304 Addition of phenylalanine increased chelating groups which increased adsorption efficiency of  
305 clays.  
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308 **Fig. 8.** Effect of stirring time on the adsorption of Fe and Mn using unmodified clay A and B.  
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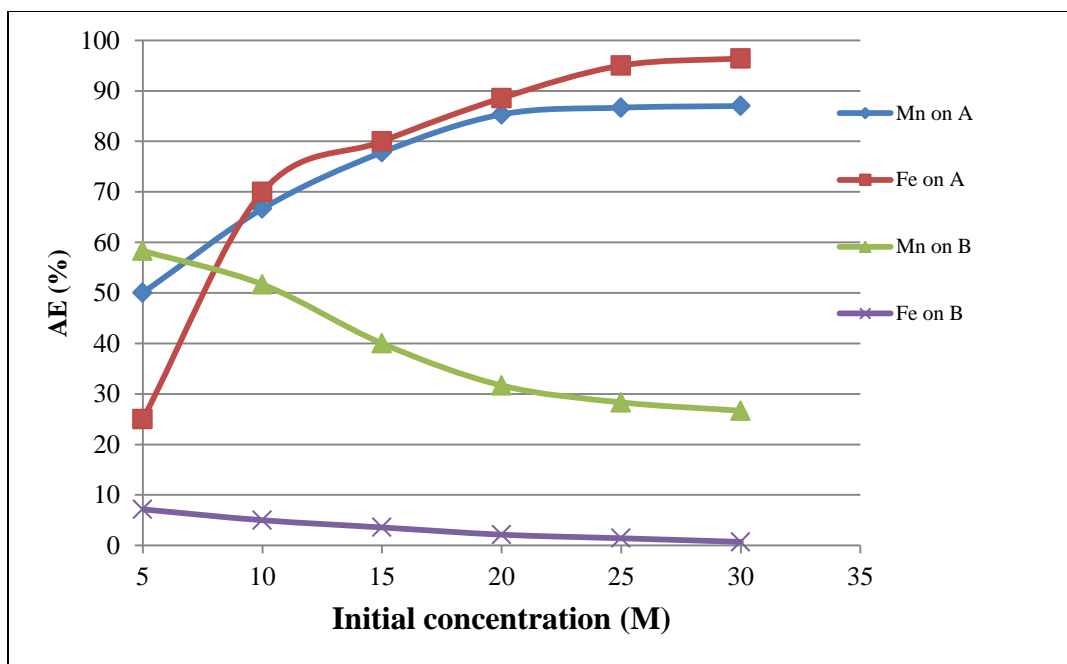


310  
 311 **Fig. 9.** Effect of stirring time on adsorption of Fe and Mn using modified clay A and B.  
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313 *Effect of Initial Concentration on Adsorption of Clays A and B*

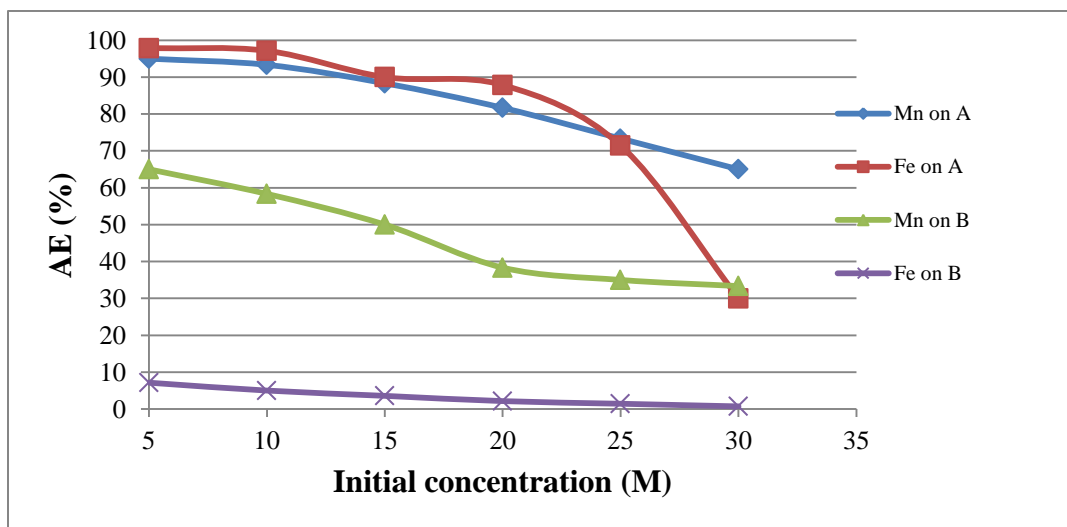
314 The effect of initial concentration of the adsorption of Fe and Mn was also studied.  
 315 Solutions containing high concentrations of Fe and Mn increased the competition for adsorption  
 316 due to saturation at active surface sites [1]. Therefore, increasing initial concentration decreased  
 317 the adsorption efficiency (Fig. 10 and Fig. 11). This is contradictory to other studies where  
 318 increase in initial concentration increases adsorption efficiency of adsorbent [18]. However, a  
 319 different trend was observed in unmodified black clay where adsorption efficiency increased  
 320 with an increase in initial concentration. This was explained by the high diffusion rate from the  
 321 bulk solution into the adsorption active sites of the adsorbent. Also more active sites available  
 322 since black clay has more silicate and aluminate content than the clay B which are responsible  
 323 for chelation of metal ion.





324  
 325 **Fig. 10.** Effect of initial concentration on the adsorption of Fe and Mn using unmodified clay A  
 326 and B.

327

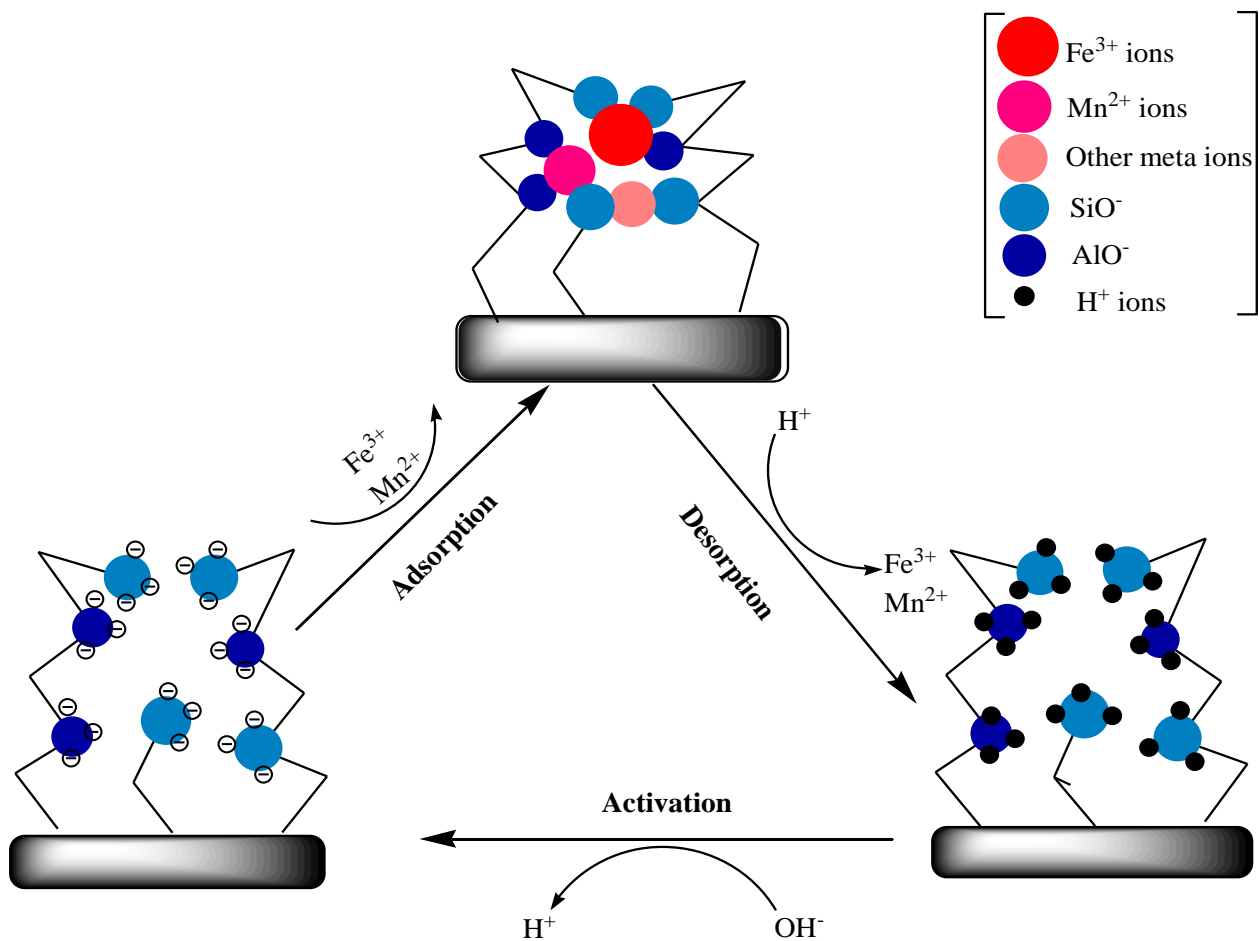


328  
 329 **Fig. 11.** Effect of initial concentration on the adsorption of Fe and Mn using modified clay A and  
 330 clay B.

331

332 The proposed mechanism for the adsorption of the metals on the clays is as follows:  
 333 When clays are purified with H<sub>2</sub>SO<sub>4</sub>, The metal ions including Fe<sup>3+</sup> and Mn<sup>2+</sup> which are naturally  
 334 bound to the adsorption sites of the clays are washed away (Fig. 12). The positively charged

335 protons have strong electrostatic interaction with the electron rich  $\equiv\text{SiO}^-$  and  $\equiv\text{AlO}^-$ , as a result,  
 336 the protons replace the metal ions from the surface of the clay adsorbent. To activate the  
 337 adsorbent, NaOH is added to neutralize the protons bound on the surface of the adsorbent, hence  
 338 increase the electron density on the electron rich atoms (Fig. 12). The active surface is then used  
 339 for adsorption purposes.



340  
 341

342 **Fig. 12.** Schematic diagram for adsorption mechanism the metals on the clays.

343  
 344

#### *Adsorption Capacity of the Clays*

345 The adsorption capacities of unmodified and modified clay (A and B) were evaluated for  
 346 adsorption of Fe and Mn from simulated samples at optimum conditions. The adsorption was  
 347 found to increase significantly on functionalized clays (Table 4 and Table 5). Functionalization  
 348 of these clays with phenylalanine increased the binding sites of the metals due to introduction of  
 349 chelating groups (amino and carboxylic groups); hence improve metal removal from solutions.

350 Table 4: Holding capacity of unmodified black (A), and yellow (B) clay at optimized parameters.

| Analyte | Trials | Black Clay (A)   |   | Yellow Clay (B)  |   |
|---------|--------|------------------|---|------------------|---|
|         |        | mass of clay (g) | $m_{\text{adsorbate}}/m_{\text{adsorbent}}$<br>(mg/g) | mass of clay (g) | $m_{\text{adsorbate}}/m_{\text{adsorbent}}$<br>(mg/g) |
| Mn      | 1      | 1.0156           | $0.113 \pm 0.000$                                     | 1.0124           | $0.121 \pm 0.002$                                     |
|         | 2      | 1.0124           |   | 1.0216           |   |
|         | 3      | 1.0139           |   | 1.0094           |   |
| Fe      | 1      | 1.0374           | $0.030 \pm 0.001$                                     | 1.0221           | $0.011 \pm 0.001$                                     |
|         | 2      | 1.0286           |   | 1.0315           |   |
|         | 3      | 1.0412           |   | 1.0267           |   |

351

352 Table 5: Holding capacity of modified black (A), and yellow (B) clay at optimized parameters.

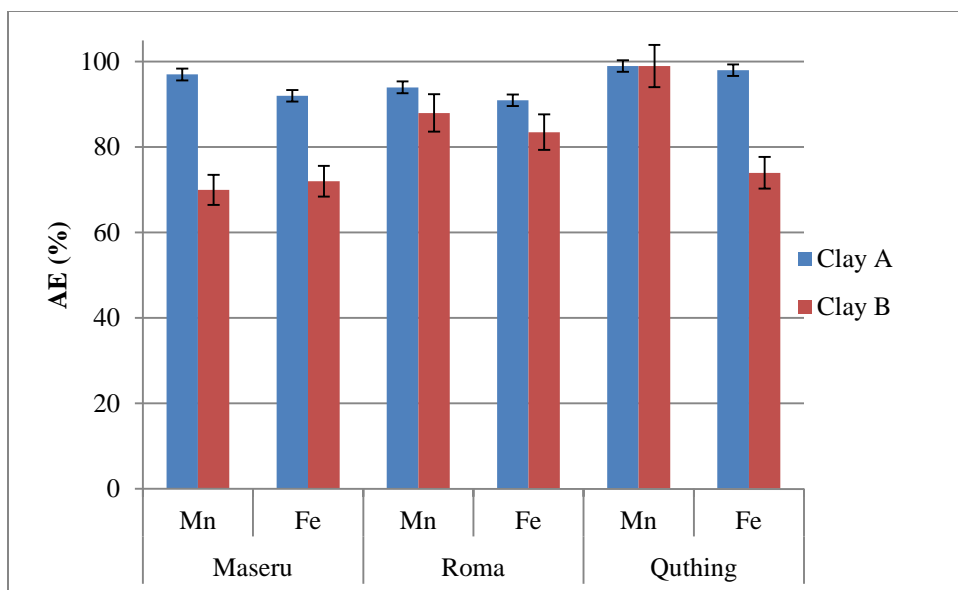
| Analyte | Trials | Clay A           |   | Clay             |   |
|---------|--------|------------------|---|------------------|---|
|         |        | Mass of clay (g) | $M_{\text{adsorbate}}/m_{\text{adsorbent}}$<br>(mg/g) | Mass of clay (g) | $M_{\text{adsorbate}}/m_{\text{adsorbent}}$<br>(mg/g) |
| Mn      | 1      | 1.0142           | $0.128 \pm 0.0011$                                    | 1.0134           | $0.138 \pm 0.003$                                     |
|         | 2      | 1.0241           |   | 1.0156           |   |
|         | 3      | 1.0182           |   | 1.0125           |   |
| Fe      | 1      | 1.0169           | $0.0398 \pm 0.0003$                                   | 1.0165           | $0.030 \pm 0.001$                                     |
|         | 2      | 1.0112           |   | 1.0158           |   |
|         | 3      | 1.0125           |   | 1.0119           |   |

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354

#### *Adsorption on Real Water Samples*

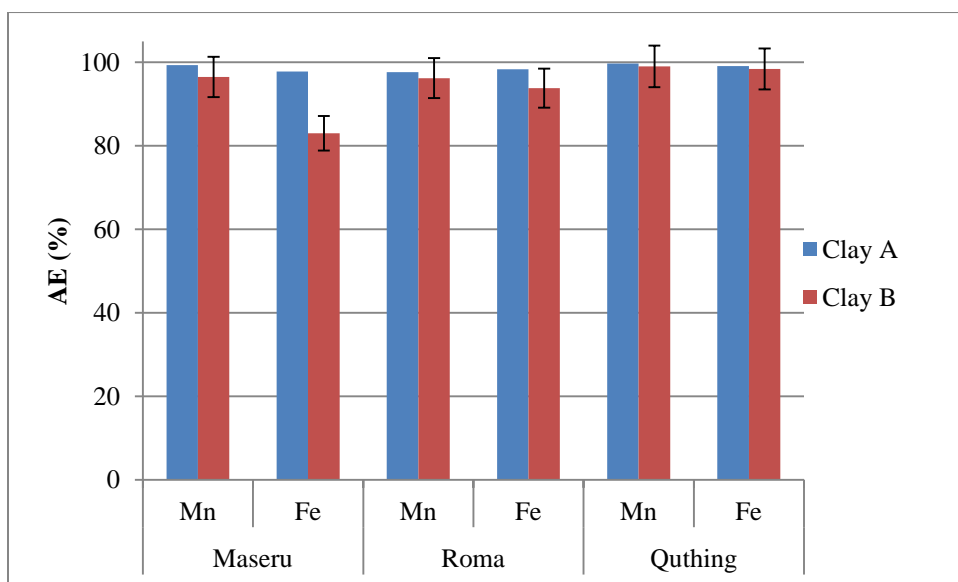
355 Following the optimization the clay samples and their high capacity to adsorb Fe and Mn  
 356 ions from simulated water samples, the clays were used in a batch reactor to remove these metals  
 357 from real water samples. The adsorption efficiency of the clay obtained from Maseru sample was  
 358 found to be lower than that of clays obtained from Quthing and Roma (Fig. 13 and Fig. 14). This  
 359 observation was attributed to the saturation of the adsorption sites of the clays from Maseru  
 360 samples because the water contained higher concentrations of Fe and Mn than the other two  
 361 samples.



362

363 **Fig. 13.** Adsorption of Mn and Fe on real samples using unmodified clay A and B.

364



365

366 **Fig. 14.** Adsorption of Mn and Fe on real samples using modified clay A and B.

367

368 Clay A was observed to have the highest adsorption of Fe and Mn compared to clay B on  
 369 real samples obtained from the three water sources (Fig. 13). This could be due to high level of  
 370 adsorption active surface sites present in clay A relative to clay B. Functionalization of all these  
 371 clays with phenylalanine increased their adsorption efficiency (Fig. 14) as shown by the  
 372 increased removal of Fe and Mn from the water samples.

373 Adsorption was significant enough to the give treated water an acceptable aesthetic  
374 appearance (Fig. 14). The concentrations of Fe detected in Maseru, Roma and Quthing samples  
375 were found to be 3.15 ppm, 2.99 ppm and 2.31 ppm respectively. The adsorption efficiencies  
376 using modified clay A were found to be 97.8%, 98.1% and 98.4% while using clay B, they were  
377 found to be 85.5%, 94.2%, 98.2%. The concentrations of Mn detected in Maseru, Roma and  
378 Quthing samples were found to be 1.201 ppm, 1.527 ppm and 1.754 ppm respectively. The  
379 following adsorption efficiencies were obtained 98.5%, 97.9%, 100% when using clay A and  
380 97.6%, 96.1%, 98.9% when using clay B. The amount of Fe and Mn adsorbed and the adsorption  
381 efficiencies on Fig 14 are key explanations for the aesthetic appearance of the treated water (Fig.  
382 15).

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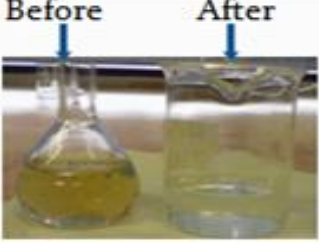
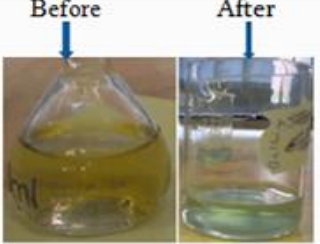
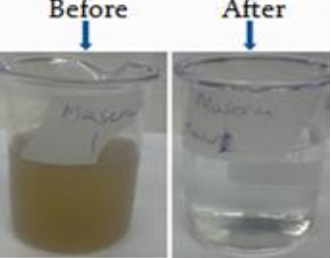
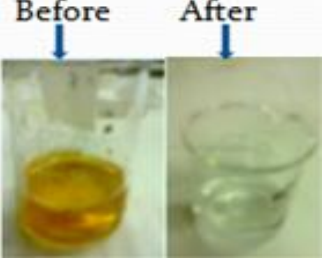
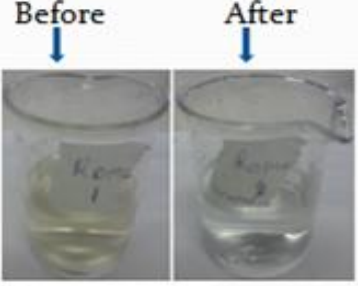
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|  |   |
|--|---|
|                               |                               |
| <p>A picture taken before and after adsorption of Fe from Fe standard solution using black clay.</p>           | <p>A picture taken before and after adsorption of Mn from Mn standard solution using black clay.</p>            |
|                               |                               |
| <p>A picture taken before and after adsorption of heavy metals present in Maseru samples using black clay.</p> | <p>A picture taken before and after adsorption of heavy metals present in Quthing samples using black clay.</p> |
|                             |   |
| <p>A picture taken before and after adsorption of heavy metals present in Roma samples using black clay.</p>   |   |

400 **Fig. 15.** Aesthetic appearance of water samples before and after treatment using modified black  
 401 clay.

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#### *Kinetic Studies*

404

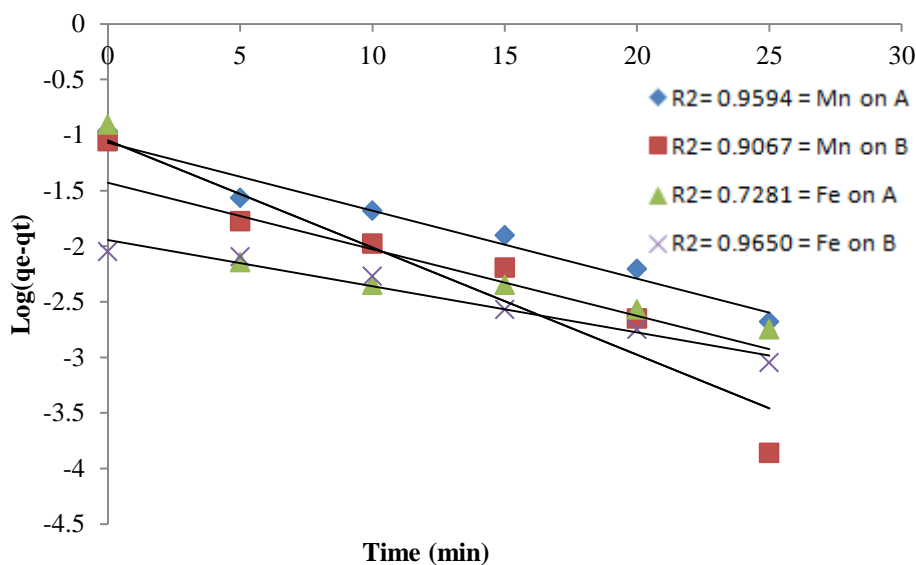
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The kinetic studies for the adsorption of the metals on clay A and B was modeled using Pseudo first order kinetics and Pseudo second order kinetics. The linear graphs were plotted and the correlation coefficient ( $R^2$ ) values were calculated from the slopes of the graphs (Figs. 16, 17,

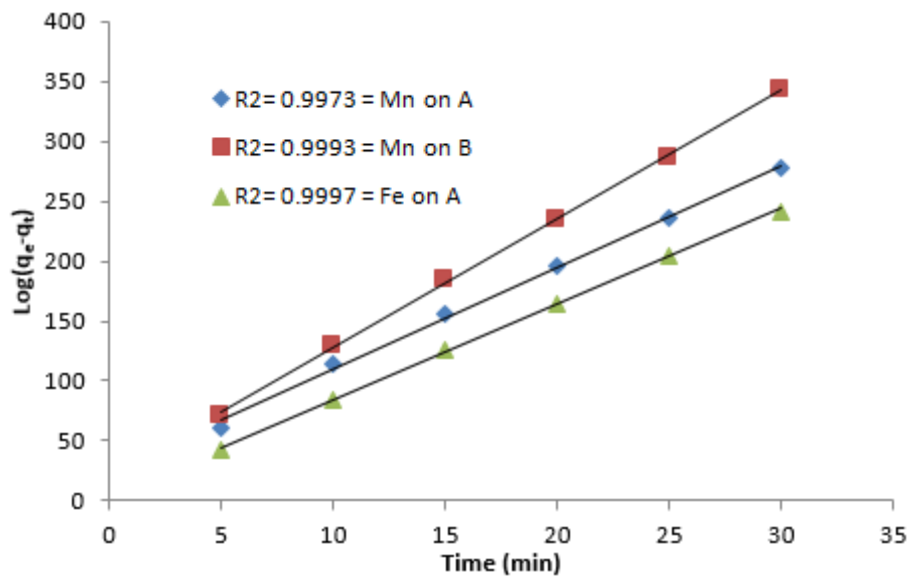
407 18, 19). The  $R^2$  values of Pseudo second order kinetics were generally higher than those of the  
 408 Pseudo first order kinetics except for the adsorption of Fe on unmodified red (clay B), Fe on  
 409 modified black clay (clay A) and Mn on modified red clays (clay A) (Table 6). This meant that  
 410 the adsorption of Mn and Fe on both clays (modified and unmodified) was favoured by the  
 411 Pseudo second order kinetics except for the adsorption of Fe on unmodified red (clay B), Fe on  
 412 modified black clay (clay A) and Mn on modified red clays (clay A) which was favoured by  
 413 Pseudo first order kinetics.

414



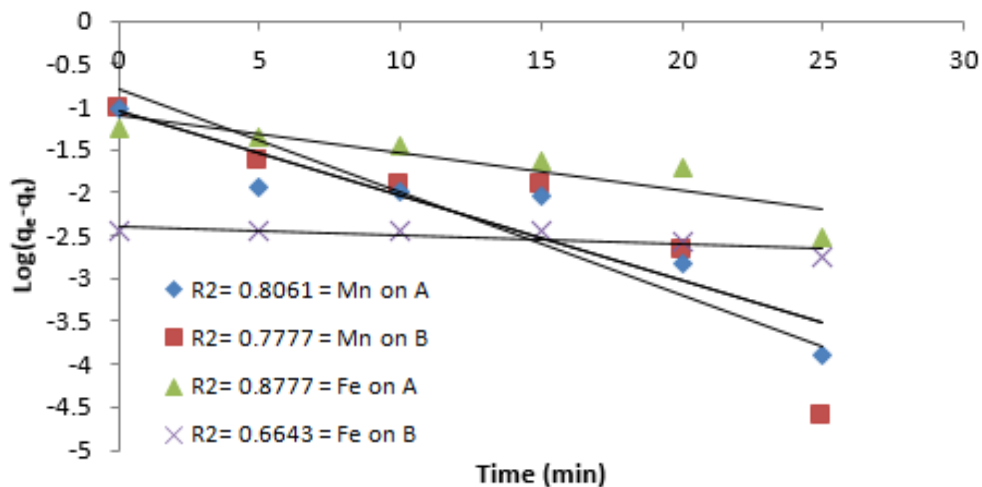
426 **Fig. 16.** The Pseudo first order kinetics for the adsorption of Mn and Fe on unmodified clay A  
 427 and clay B.

428



429  
 430 **Fig. 17.** The Pseudo second order kinetics for the adsorption of Mn and Fe on unmodified clay A  
 431 and B. The plot of Fe on unmodified clay B is not shown because no adsorption of Fe occurred  
 432 in the first 15 min.

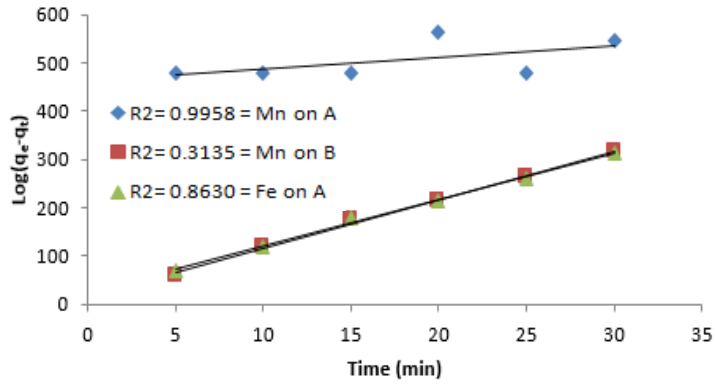
433



434  
 435 **Fig. 18.** The Pseudo first order kinetics for the adsorption of Mn and Fe on modified clay A and  
 436 clay B.

437





438

439 **Fig. 19.** The Pseudo second order kinetics for the adsorption of Mn and Fe on modified clay A  
 440 and B. The plot of Fe on modified clay B is not shown because no adsorption of Fe occurred in  
 441 the first 15 min.

442

443 Table 6: The correlation coefficients for the kinetic studies of clay A and B.

| Clays                   | Mn <sup>2+</sup>                    |                                     | Fe <sup>2+</sup>                    |                                     |
|-------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
|                         | R <sup>2</sup> <sub>1st order</sub> | R <sup>2</sup> <sub>2nd order</sub> | R <sup>2</sup> <sub>1st order</sub> | R <sup>2</sup> <sub>2nd order</sub> |
| A <sub>unmodified</sub> | 0.9594                              | 0.9973                              | 0.7281                              | 0.9997                              |
| B <sub>unmodified</sub> | 0.9067                              | 0.9993                              | 0.9650                              | 0.2101                              |
| A <sub>modified</sub>   | 0.8067                              | 0.9958                              | 0.8777                              | 0.8630                              |
| B <sub>modified</sub>   | 0.777                               | 0.3135                              | 0.6643                              | 0.9867                              |

444

445

## CONCLUSIONS

446

447         This study was aimed at determining the adsorption efficiency of Fe and Mn onto two  
448 different types of clays (black and yellow clays) obtained from three sites in Lesotho. These  
449 clays were demonstrated to be suitable for removal of Fe and Mn metals from drinking water  
450 sources. The clays are relatively cheap and more abundant than conventional adsorbents used  
451 such as activated carbon, aluminium sulfate, aluminium hydroxide, *etc.*, in Lesotho. The  
452 functionalization of the clays with phenylalanine resulted in their improved adsorption efficiency  
453 and the water produced presented acceptable aesthetic appearance with very low untreated metal  
454 concentration; within the international guidelines. It was also found that increasing pH of the  
455 water samples and the stirring time resulted in increased adsorption efficiency of the clays until  
456 equilibrium was reached. Increasing the initial concentration decreased adsorption efficiency due  
457 to the fast depletion of vacant active surface sites for adsorption. The clays investigated were  
458 found to be effective on removal of Mn and Fe from the real water samples with up to 99.7%  
459 after modification with phenylalanine. The use of these clays can be a viable solution to low  
460 income economies since the clays are present in abundance. The clays could be mined and used  
461 as adsorbent based filters for domestic water supply in Lesotho.

462

463

## ACKNOWLEDGEMENTS

464

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467 Africa's Science Campus. Support from these organizations is acknowledged.

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