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# Study on simultaneous adsorption of phosphate and fluoride from water environment by modified laterite ore from Northern Vietnam

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**Abstract:** Natural laterite can be regarded as a strong adsorbent due to its special structure and composition. In this study, the laterite was modified by manganese oxide ( $\text{MnO}_2$ ) to create a new good adsorbent for treating phosphate and fluoride in water environment. Under the optimized conditions of the adsorbent dose (pH 6, temperature  $20^\circ\text{C}$ , and the contact time 180 min), laterite, doped manganese, with diameter of grains from 0.1 to 0.5 mm has maximum adsorption capacity of 31.25 mg/g and 10.99 mg/g for phosphate and fluoride, respectively. The characteristics of the manganese doping laterite were confirmed using various techniques like SEM, BET, XRD, EDX. The adsorption process of the material was investigated by both kinetic models (pseudo-first and second orders) and isotherm models (Freundlich and Langmuir). This new material was tested for treatment of wastewater taken from the superphosphate fertilizer factory, with the results obtained showing high potential for application in reality.

**Keywords:** adsorption; dope; fluoride; laterite ore; manganese dioxide; phosphate.

## 1 Introduction

Phosphate and fluoride are well known as essential elements for living organisms. Nevertheless, to date, the increasing release of phosphate or fluoride-containing wastewater from industrial activities, specially semiconductor, electroplating, glass, steel, ceramic, and fertilizer industries has deteriorated ecosystems and caused water-quality problems [1–3]. Therefore, developing

high effective technologies based on precipitation, ion exchange, adsorption, reverse osmosis, and nanofiltration have been studied for removal of phosphate or fluoride from wastewater. Among various available technologies for decontamination of phosphate or fluoride, the adsorption method is relatively simple, economical, and highly efficient [4, 5]. Laterite, a kind of leached soil of the humid tropics, was found to be a suitable low-cost adsorbent in adsorbing either phosphate or fluoride from water environment. Chemical compositions of laterite depend on the composition of parent rock, geographical depth, and climatic conditions [6–8]. The main composition of laterite is iron, aluminum oxides. Previous studies showed the effectiveness of this ore in removing phosphate when used in wetland systems [9]; otherwise, this ore was also studied to remove fluoride from contaminated drinking water [10]. In addition, in natural waters, manganese (hydr)oxides are found in combination with other metal to form composite oxides [11, 12]. Therefore, they are widely used in water and wastewater treatments, due to their affinity toward fluoride and phosphate [13–15]. Several studies have shown that the manganese compounds are nonhazardous, insoluble, and efficient sorbents [16] for removing either phosphate or fluoride removal: Fe-Mn binary oxide [17, 18], Fe-Al-Mn trimetal oxide [19],  $\text{MnO}_2$ -coated alumina [20–23], bentonite clay with incorporated  $\text{MnO}_2$  [24],  $\text{MnO}_2$ -coated activated carbon [25],  $\text{KMnO}_4$ -modified activated carbon [26], and hydrated oxides of manganese ores [27].

Using the low-cost ore is a general trend in developing adsorbents for treating contaminants [28–30]. Hence, a few investigations use modified laterite ore as adsorbents; for example, Maiti et al. reported the production of a treated laterite, which is a material produced by a two-step process [31]. In this study, manganese-doped laterite (MDL) was, therefore, utilized as adsorbents to remove simultaneously both phosphate and fluoride in aqueous environment. The several factors relating to the adsorption capacity of MDL, such as manganese spiking portion, characterization, equilibrium time, initial pH, dosage, and coexisting ions, were investigated systematically. The adsorption isotherms and kinetics of MDL were also studied in detail.

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## 2 Materials and methods

### 2.1 Reagents

The laterite ore was collected from Thach That province, Northern Vietnam, and washed with distilled water to remove the earthy substance. It was then dried at room temperature and crushed to particle sizes of 0.1–0.5 mm.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the ore were quantified by ICP-MS equipment (Perkin Elmer ELAN 9000, USA), and their average amounts are approximately 20.5% (for  $\text{Fe}_2\text{O}_3$ ) and 13.8% (for  $\text{Al}_2\text{O}_3$ ).

All chemical reagents used in the experiments were of analytical grade purchased from Merck (Germany), mainly including manganese oxide ( $\text{MnO}_2$ ), sodium hydrate ( $\text{NaOH}$ ), anhydrous sodium phosphate ( $\text{Na}_3\text{PO}_4$ ), sodium fluoride ( $\text{NaF}$ ), sodium chloride ( $\text{NaCl}$ ), and hydrochloric acid ( $\text{HCl}$ ). Deionized water from Milli-Q water purification system was used throughout all experiment processes of this study.

### 2.2 Preparation of $\text{Mn}^{4+}$ -doped laterite ore

The surface layers of the laterite grains do not usually contain a necessary concentration of metal ions ( $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ) for the modifying procedure of laterite. Therefore, before doping manganese on laterite, fresh layers containing a higher concentration of these metals are regenerated onto the surfaces of laterite grains. The laterite grains were shaken in  $\text{HCl}$  solution for a part of the metal ions from the laterite to be dissolved in the solution. The dissolved ions are then co-precipitated in the form of their (hydr)oxides by alkaline solution, and the hydrolyzed products are setting onto the granule surface over the time. By this way, the new fresh layer of laterite was created. The material was filtered, dried at a temperature lower than  $70^\circ\text{C}$ , and washed out of  $\text{NaCl}$ , and then dried again in the same above-mentioned condition.

Manganese is doped into the fresh laterite layer by the same way creating the fresh layer, but instead of co-precipitation of only the shaken solution, certain amount of  $\text{Mn}^{4+}$  was added and well mixed, and as a result, the metals' ions were co-precipitated by the  $\text{NaOH} + \text{H}_2\text{O}_2$  solution.

### 2.3 Estimation of amount of phosphate and fluoride ions adsorbed by MDL

The concentrations of phosphate and fluoride were analyzed according to Standard Methods for the Examination of Water and Waste Water Fluoride: SMEWW 4500 – F<sup>-</sup>. B&D:2012; Phosphate: SMEWW 4500 – P.E: 2012. MDL was added to a solution containing phosphate (10 mg/l) and fluoride (5 mg/l). After, the solution was stirred for 2 h at  $25^\circ\text{C}$  and a pH of 6.0. The solution was then analyzed for the concentration of phosphate and fluoride by the absorption spectrophotometer (880 nm for phosphate and 570 nm for fluoride, UV-Vis 2450, Shimadzu, Japan). The amount of phosphate and fluoride ions adsorbed onto the adsorbent at equilibrium was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g);  $C_0$  is the initial concentration (mg/l);  $C_e$  is the equilibrium concentration (mg/l);  $V$  is the volume of the solution; and  $W$  is the weight of the adsorbent (g).

### 2.4 Properties of $\text{Mn}^{4+}$ -doped laterite ore

Characteristics of the adsorbents were investigated by several techniques. The surface morphology of the natural and modified laterite ores were indicated by a scanning electron microscope (SEM). The specific surface area was measured by the BET surface area analyzer. The X-ray diffraction (XRD) analysis of the adsorbent material was carried out by the powder XRD technique. The elements of the material were detected by energy-dispersive X-ray (EDX) technique.

### 2.5 Adsorption pseudo-first and pseudo-second orders

In order to study adsorption dynamics, phosphate solutions of 10, 20, and 50 mg/l and fluoride solutions of 10, 15, and 20 mg/l concentrations were investigated at the initial pH value of 6.0. One hundred milliliters of both phosphate- and fluoride-containing solution was stirred with a definite amount of adsorbent for different time durations ranging from 60 to 300 min at pH of 6.0. After the contact time, the adsorbent was separated from the solution by filtration, and the remaining concentration of phosphate and fluoride in the solution was determined.

### 2.6 Adsorption Langmuir and Freundlich isotherm

Phosphate and fluoride (named adsorbates) adsorption isotherms on MDL at a pH value of 6.0 were studied at different temperatures ( $20^\circ\text{C}$ ,  $30^\circ\text{C}$ , and  $40^\circ\text{C}$ ) by varying the initial concentrations of both phosphate and fluoride. In each experiment, 1 g of the adsorbent was transferred into a 250-ml conical flask, and 100 ml of solution containing different concentrations of adsorbates was then added to the flask. After the reaction period, all samples were filtered by a Whatman 0.45- $\mu\text{m}$  membrane filter, and the concentrations of the adsorbates were analyzed. The amounts of adsorbed phosphate or fluoride were calculated by the difference of the initial and residual amounts of phosphate or fluoride in solution divided by the weight of the adsorbent.

## 3 Results and discussion

### 3.1 Investigating conditions for creating fresh laterite layer

The optimal conditions for creating the fresh laterite layers containing a higher concentration of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions are dependent on the concentration of  $\text{HCl}$  and shaking time. In this study, the laterite grains with a size

of 0.1–0.5 mm diameter were shook in 100 ml of various concentrations of HCl (3.0–6.0 M) for a shaking time period from 1 to 6 h. The results are given in Supplemental Figure S1.

Our previous study [32] showed that the very thin fresh laterite layer coated with calcined laterite grains is a good adsorbent for some ions, when the ratio of the fresh laterite layer and calcined laterite grains (0.1–0.5 mm in diameter) is about 0.5–0.7/1000. In an HCl concentration of 4 M and a shaking time of 3 h, concentrations of Fe and Al are suitable for the optimal fresh laterite layer (Supplemental Figure S1); therefore, these conditions are chosen for laterite modification.

### 3.2 Influence of manganese spiking portion on adsorption capacity of the material

In order to choose the most optimal modified material for the removal of phosphate and fluoride, manganese was added with various molar ratios between  $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$ , which was dissolved from the laterite into the solution. MDL – 0 was without  $\text{Mn}^{4+}$  doped onto the surface of the laterite; MDL 1:3, 1:2, 1:1, 2:1, and 3:1 were ratios of molar between  $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$  covered on the surface of the laterite, respectively.

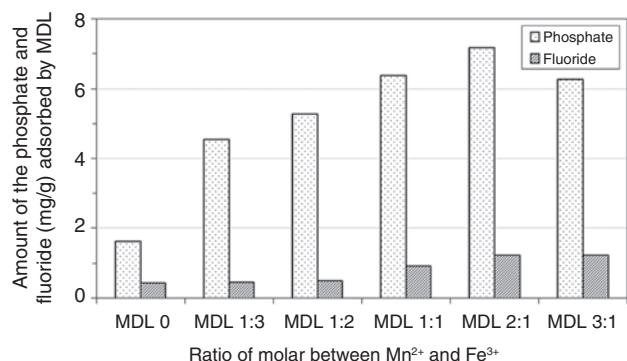
Concentrations of phosphate and fluoride were used for investigating the adsorption capacity of the materials to be 10 and 5 mg/l, respectively. The amount of the material in the solution was 1.0 g per 100 ml, and contact time was 180 min.

The results in Figure 1 show that manganese strongly influences both the phosphate and fluoride adsorption capacity of the material. Increasing the ratio between manganese and iron in the laterite layer until it equal to 2:1 leads to the increase in the material adsorption

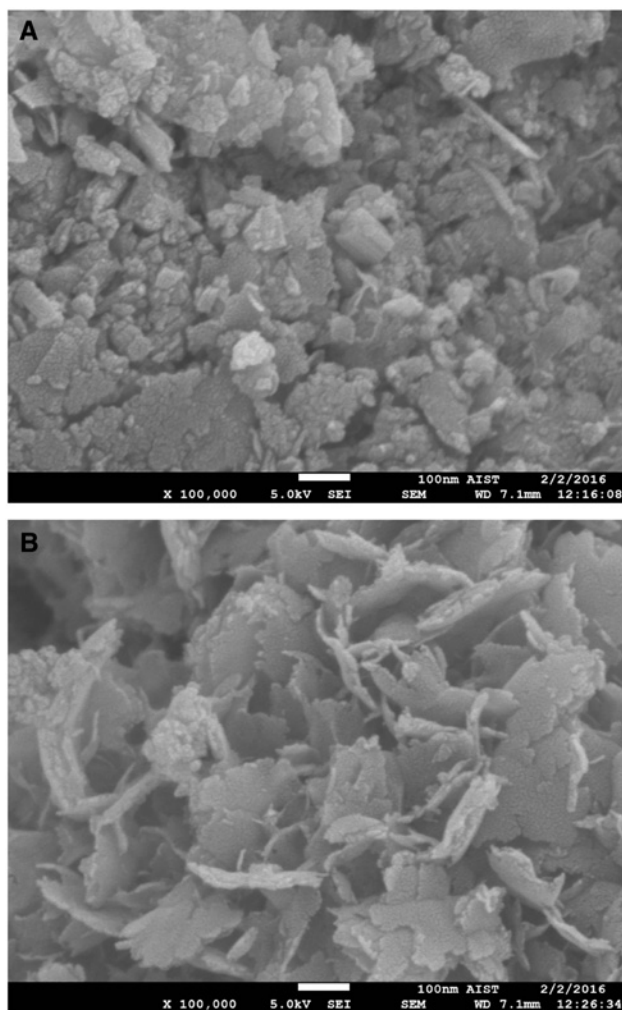
capacity with respect to both the simultaneous phosphate and fluoride. At a higher ratio, the material's adsorption capacity decreases. The reason could be that, when manganese dioxide inserts into  $\text{Fe}^{3+}$  hydroxide net, as the affinity of manganese for oxygen is higher than that of iron, manganese attracts oxygen to its side. A slightly positive effect on the adjacent iron atom appears, and as a result, an anion adsorption center appears. When the manganese portion is high (3:1 for instance), the positive effect may be reduced because the precipitated  $\text{MnO}_2$  molecules form their own clusters and lessen their attraction for oxygen atoms of other metals. For fluoride anion, it is different. From the obtained results and as discussed above, the material M2:1, named as MDL, was chosen for adsorbing phosphate and fluoride in further investigations.

### 3.3 Characterization of the material

The SEM technique enables the direct observation of any microstructural changes on the surface of the laterite ore that might have occurred due to modification. The SEM images in Figure 2A, B indicate the surface morphology of the natural laterite and MDL. The natural laterite surface includes small particles with significantly different sizes (Figure 2A). By contrast, the MDL has a more comparatively porous and uniform surface (Figure 2B). The characteristic of the MDL was analyzed by the EDX technique. Besides, the EDX spectrum presents that the major components of the MDL surface contain Al, Fe, Mn, and O with the amount of each to be approximately 17%, 9%, 5%, and 36%, respectively (Supplemental Figure S2). The results indicate that manganese exists on the surface of the material. Consequently, doping manganese affected not only the morphology but also the surface area of the laterite ore. The surface analysis of laterite and MDL was measured using the BET surface area analyzer and were found to be approximately 17.8  $\text{m}^2/\text{g}$  and 74.3  $\text{m}^2/\text{g}$ , respectively. The pore volumes of laterite and MDL were 0.02  $\text{cm}^3/\text{g}$  and 0.28  $\text{cm}^3/\text{g}$ , respectively. The surface area of MDL is increased by a factor of more than 4 compared to the laterite; while the pore volume is approximately 10 times. The XRD patterns of the natural laterite and MDL are shown in Figure 3A, B, respectively. Manganese was not found in the component of the natural laterite (Figure 3A), but the amount of manganese in the MDL is shown in Figure 3B. Therefore, the XRD study reveals that the structure of adsorbent was changed after the doping procedure of manganese.



**Figure 1:** Influence of manganese spiking portion on the material adsorption capacity.



**Figure 2:** SEM images of before and after the denaturing process of laterite ore: (A) natural laterite ore, (B) manganese-doped laterite.

### 3.4 pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of MDL

The pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ) is an important interfacial parameter used widely in characterizing the ionization behavior of a surface. This point of the material was investigated as follows: 0.2 g of the adsorbent was transferred into 250-ml conical flasks containing 50 ml of 0.01 M NaCl solution. These solutions were adjusted to varied initial pH values (2.0–12.0) by 0.1 M  $\text{HNO}_3$ . This setup was kept for 48 h, and then, the adsorbent was filtered out of the NaCl solutions by a Whatman 0.45- $\mu\text{m}$  membrane filter, and the final pH values of the solutions were measured. The initial and final pH values of the solutions were measured as  $\text{pH}_{\text{initial}}$  and  $\text{pH}_{\text{final}}$ , respectively.  $\text{pH}_{\text{PZC}}$  is the intersection point of the lines joining the pH initial and  $\text{pH}_{\text{final}}$  in “ $\text{pH}_{\text{final}}$  vs.  $\text{pH}_{\text{initial}}$ ” graph. The  $\text{pH}_{\text{PZC}}$  of MDL was found to be approximate 7.1.

### 3.5 Determination of optimal pH for adsorbing phosphate and fluoride by MDL

The initial concentrations of phosphate and fluoride for this study were 10 and 5 mg/l respectively; the contact time was 180 min, and the pH value varied from 4 to 9. In the solution with pH lower than 5, the hydrogen ion concentration is high enough to act on the hydroxide radicals on the surface of the fresh laterite layer and increase their solubility; this results in a decrease in the adsorption capacity of the material. On the other hand, the adsorption of the surveyed anions also decreases at a pH higher than 7, but the reason is deferent: it is the adsorption competition of the hydroxyl ions in the solution. Therefore, the optimum pH range for both phosphate and fluoride ions are from 5.0 to 7.0 (Supplemental Figure S3). These results are the same as those of many studies for adsorbing either phosphate or fluoride [33–36]. The pH 6 will be used for further experiments.

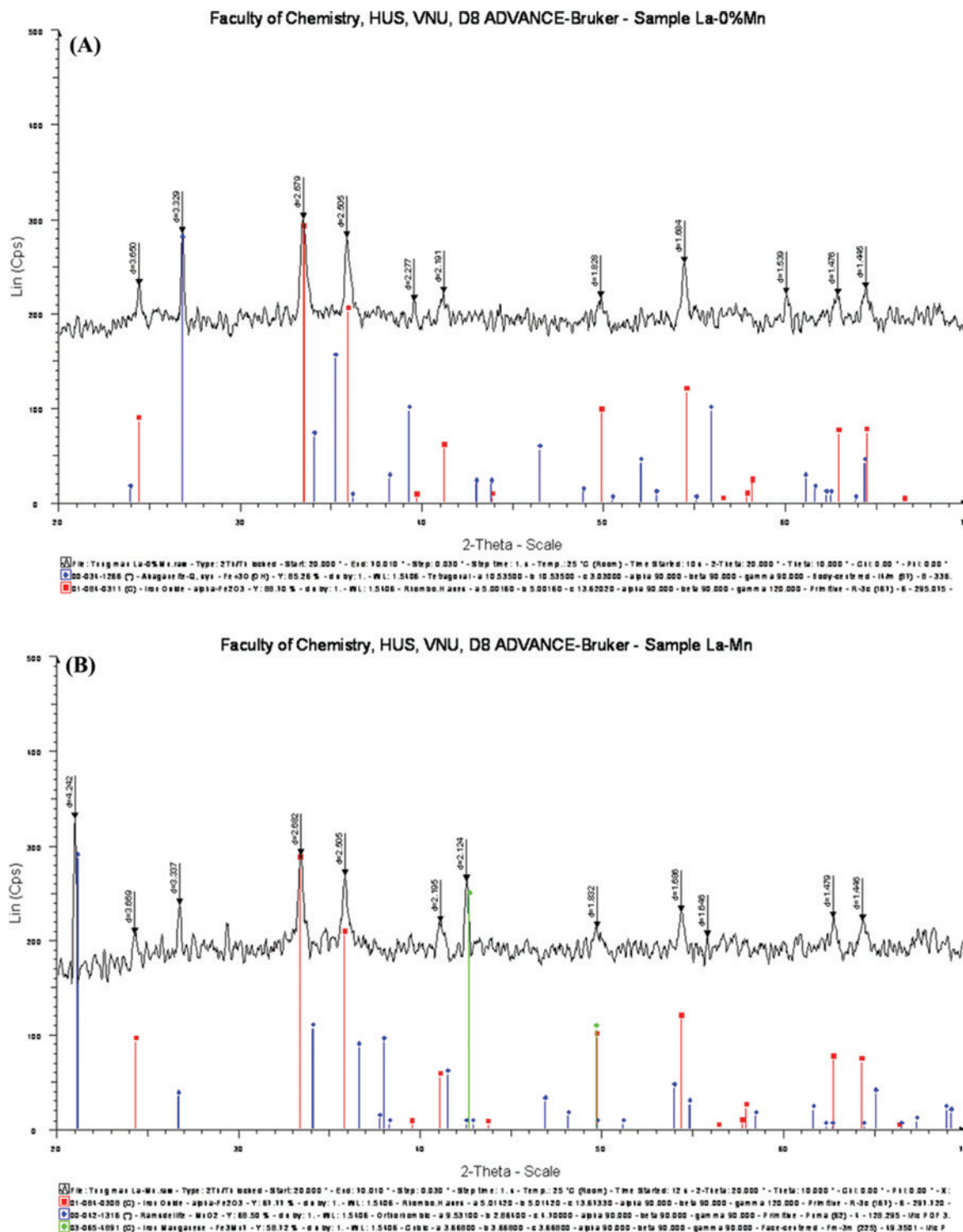
### 3.6 Determination of adsorption equilibrium time

To investigate equilibrium time, initial concentrations of phosphate and fluoride were taken 10 and 5 mg/l, respectively; the contact time was studied from 0 to 210 min. The obtained results are described in Figure 4. The adsorption processes of MDL for phosphate reaches equilibrium status after about 120 min and that for fluoride, about 180 min (Figure 4). The equilibrium time of 180 min is, therefore, used for further investigations.

### 3.7 Effect of adsorbent dosage on removal of phosphate and fluoride

In order to find the minimum dosage of MDL for maximum adsorption of phosphate and fluoride, the effects of adsorbent dosage were measured by varying the dosages of MDL from 0.01 g to 0.11 g in aqueous solution containing phosphate and fluoride concentrations to be 10 mg/l and 5 mg/l, respectively. It was observed as shown in Figure 5 that the percentage removal increased with respect to the increased dosage and then remained constant after 0.06 g for phosphate and 0.07 g for fluoride. The increase in the adsorption capacity with an increase in dosage is apparent because any adsorption process depends upon the number of active sites [37]. An increased adsorbent dosage implied a greater surface area and a greater number of





**Figure 3:** XRD images of the natural and Mn-doped laterite ore: (red peak) iron oxide ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), (green peak) iron manganese ( $\text{Fe}_3\text{Mn}_7$ ). (A) natural laterite ore, (B) manganese-doped laterite.

binding sites available for the constant amounts of both phosphate and fluoride. The adsorbent dosage, therefore, was optimized to be 0.11 g for further experimental studies.

### 3.8 Adsorption kinetic models

The adsorption kinetics based on the adsorption capacity of MDL are described by the equations as follows.

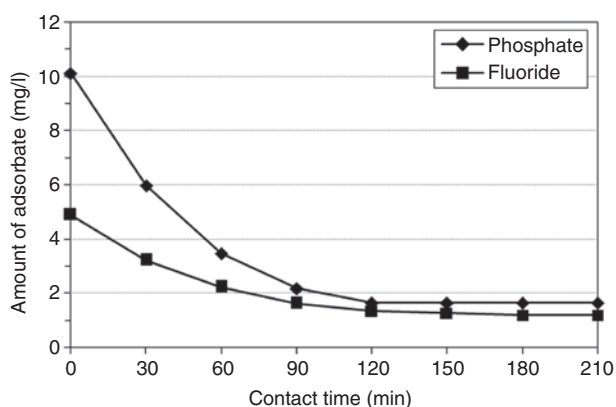


Figure 4: Determination of adsorption equilibrium time.

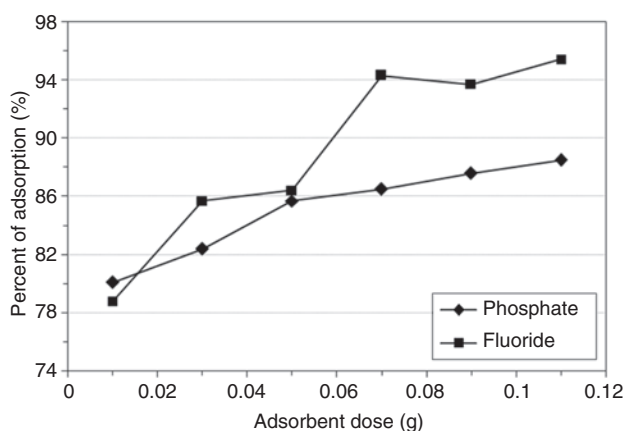


Figure 5: Effect of dosage to removal of fluoride and phosphate adsorption by MDL.

The pseudo-first order [38]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

and the pseudo-second order [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

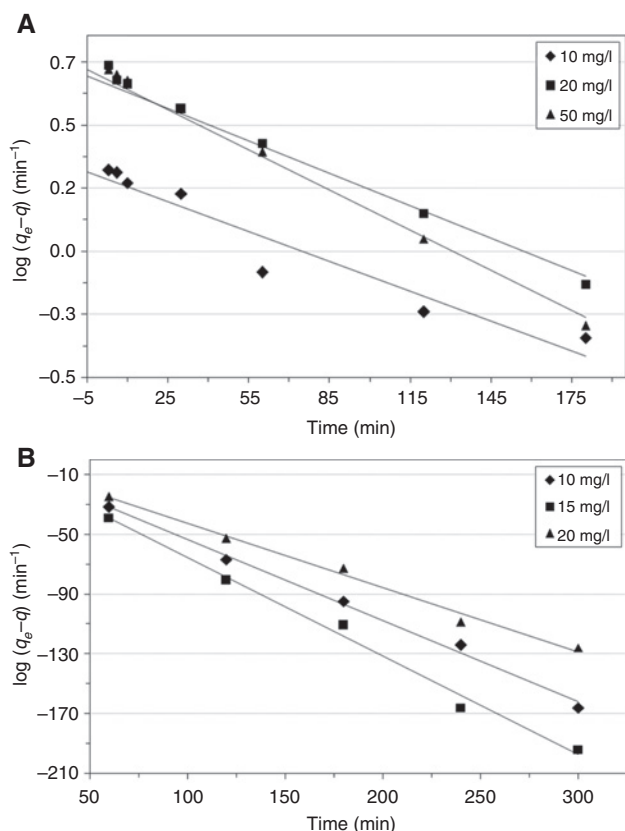
where  $q_e$  and  $q_t$  are the amount ( $\text{mg g}^{-1}$ ) of phosphate or fluoride adsorbed at equilibrium and at time  $t$ , respectively, and  $k_1$ ,  $k_2$  are the pseudo-first-order and pseudo-second rate constants, respectively.

The kinetic data based on the pseudo-first-order model for the phosphate and fluoride adsorption onto MDL are indicated in Table 1. For phosphate adsorption, the plots in Figure 6A were found to be linear with quite good correlation coefficient ( $R^2$ ). This result indicated that the phosphate adsorption onto MDL is complied with the pseudo-first-order model with the varied concentrations of phosphate. The quick removal of phosphate, which is observed from the increasing values of  $k_1$  (Table 1), presented the availability of a large number of active sites at the surface of MDL, which increases with the increase of phosphate concentration [21]. On the contrast, for fluoride adsorption, the pseudo-first-order rate constant ( $k_1$ ) does not clearly depend on varied concentration of fluoride from 10 to 20 mg/l. MDL follows first-order kinetics with good correlation ( $R^2$ ) for fluoride concentrations (Table 1 and Figure 6B). The values of  $R^2$  were found as 0.990, 0.991, and 0.994 and also the values of  $k_1$  were found as 0.990, 1.52, and 1.25  $\text{min}^{-1}$ , respectively for the selected initial concentrations of fluoride. The result have shown the applicability of the pseudo-first-order model with respect to the influence of  $\text{MnO}_2$  on MDL.

The results, studying the adsorption potential of MDL based on the pseudo-second-order model, were listed in Table 1. For phosphate removal, it is observed that pseudo-second-order kinetics shows good correlation ( $R^2$ ) (0.992, 0.990, and 0.983) and also the values of pseudo-second-order rate constant ( $k_2$ ) were calculated as 0.0061, 0.0053, and 0.0059  $\text{mg/g} \cdot \text{min}$  at the

Table 1: Parameters for pseudo-first- and pseudo-second-order models for removing phosphate and fluoride.

Concentration (mg/l)	Pseudo-first order			Pseudo-second order		
	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$	$k_2$ (g/mg · min)	$q_e$ (mg/g)	$R^2$
Phosphate						
10	0.007	1.83	0.937	0.0061	2.58	0.992
20	0.009	4.23	0.955	0.0053	3.41	0.990
50	0.012	4.44	0.976	0.0059	4.76	0.983
Fluoride						
10	0.990	1.59	0.990	0.276	4.48	0.986
15	1.52	2.07	0.991	0.401	6.99	0.979
20	1.25	5.19	0.994	1.02	8.69	0.969



**Figure 6:** Pseudo-first-order plots for Mn-doped laterite: (A) phosphate, (B) fluoride.

three selected phosphate concentrations (Table 1 and Figure 7A). On the contrary, pseudo-second-order kinetics shows quite good correlation ( $R^2$ ) for concentrations of fluoride (The values of  $R^2$  0.986, 0.979, and 0.969) (Table 1 and Figure 7B). The values of  $k_2$  were calculated as 0.276, 0.401, and 1.02  $\text{mg/g} \cdot \text{min}$  at the three selected fluoride concentrations, respectively.

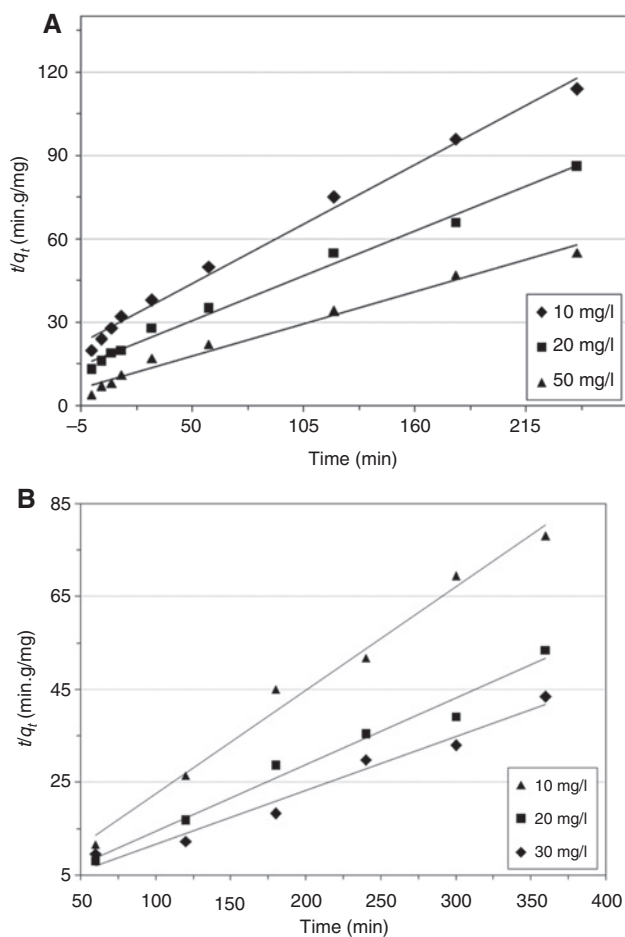
### 3.9 Adsorption isothermal models

The Freundlich and Langmuir adsorption isotherm models have been quite useful in expressing the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at a constant temperature [40–42].

The Langmuir isotherm model is as follows [43]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0},$$

and the Freundlich model is generally expressed as in the following equation [44]:



**Figure 7:** Pseudo-second-order plots for Mn-doped laterite: (A) phosphate, (B) fluoride.

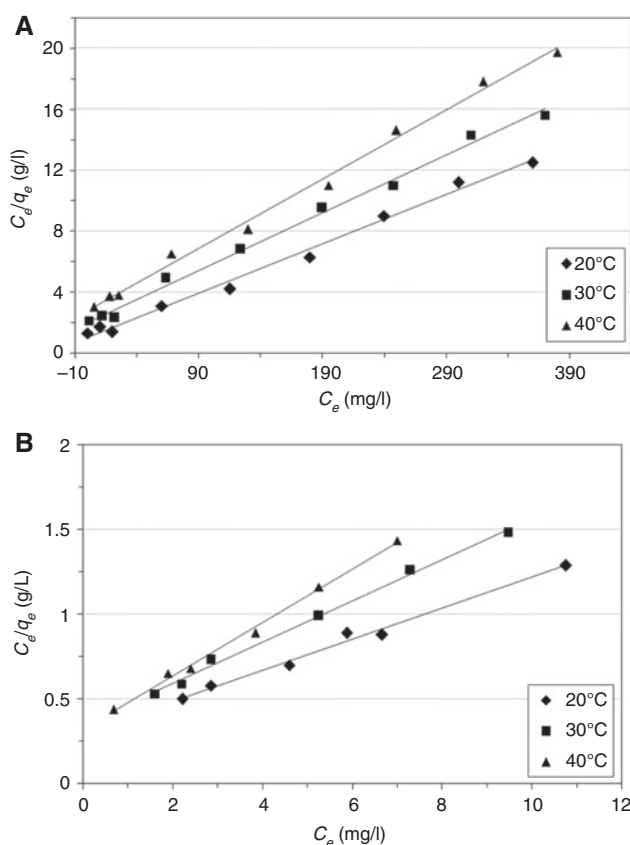
$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where  $q_e$  and  $C_e$  are the equilibrium adsorption capacity ( $\text{mg/g}$ ) and the equilibrium adsorbate concentration ( $\text{mg/l}$ ), respectively;  $q_0$  is the surface coverage ( $\text{mg/g}$ ), and  $K_L$ ,  $K_F$  are the equilibrium adsorption constants ( $\text{l/mg}$ ) of Langmuir and Freundlich models, respectively; and  $n$  was the empirical constant.

The Langmuir isotherm for phosphate and fluoride removal at three temperatures (20, 30 and  $40^\circ\text{C}$ ) given good correlation ( $R^2$ ) (Table 2 and Figure 8A, B). The  $K_L$  values for the adsorption process of phosphate decreases with a rise in reaction temperatures (Table 2). In contrast, the  $K_L$  values for the fluoride adsorption increases with increasing temperatures (Table 2). The interactions of either phosphate or fluoride with MDL indicated that the adsorption process may be exothermic for phosphate and endothermic for fluoride. Similar effects of temperature

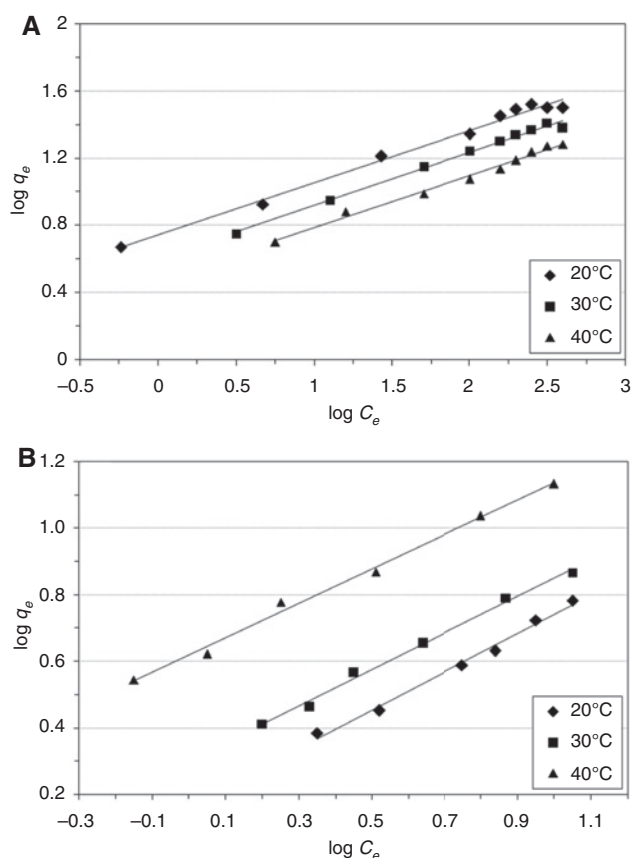
**Table 2:** Parameters for Langmuir and Freundlich isotherm models for removing phosphate and fluoride.

Temperature (°C)	Langmuir			Freundlich		
	$q_0$ (mg/g)	$K_L$ (l/mg)	$R^2$	$n$	$K_F$ (mg/g)	$R^2$
Phosphate						
20	31.25	0.031	0.992	3.23	5.52	0.990
30	27.03	0.018	0.994	3.17	3.99	0.992
40	22.22	0.016	0.994	3.24	2.99	0.990
Fluoride						
20	10.99	0.298	0.991	1.73	1.46	0.990
30	8.19	0.352	0.993	1.82	1.99	0.994
40	6.37	0.487	0.995	1.93	4.15	0.993

**Figure 8:** Langmuir isotherm plots for Mn-doped laterite: (A) phosphate, (B) fluoride.

on phosphate or fluoride were reported by other researchers [45–47].

As shown in Figure 9A, B, the plot of  $\log q_e$  versus  $\log C_e$  at different initial concentrations is linear, which confirmed the applicability of the Freundlich model for the removal of phosphate and fluoride ions of MDL. The value of  $n$  in between 1 and 10 indicates useful adsorption [46].

**Figure 9:** Freundlich isotherm plots for Mn-doped laterite: (A) phosphate, (B) fluoride.

Hence, adsorption of phosphate and fluoride on MDL may be called “useful”. The increasing values of  $K_F$  of fluoride removal with temperature indicate that adsorption is favorable at higher temperatures [48]. Many adsorbents have been tested for their phosphate/fluoride removal potentials from aqueous solutions, and some of the results were summarized in Table 3. For details, manganese was doped or modified in some material to have an adsorption capacity of phosphate from 511.3 mg/g to 313 mg/g [17–19]. Laterite ore from other areas was also used for the removal of phosphate in the range from 0.572 mg/g to 31.53 mg/g [33, 34, 49, 50]. MDL gives a phosphate adsorption capacity ranging from 22.22 mg/g to 31.25 mg/g with increasing temperature from 20°C to 40°C, as found in the present study. On the other hand, for the position of the removal fluoride, manganese was reported to be of the range from 1.43 mg/g to 11.93 mg/g [51–53], while other laterite ores have a range of fluoride removal from 0.55 mg/g to 41.01 mg/g [35, 36, 54]. However, in this study, MDL removes a fluoride in aqueous solution ranging from 5.08 mg/g to 10.99 mg/g with increasing temperature from 20°C to 40°C.



**Table 3:** Comparison between MDL and other material reported in some studies.

Adsorbents	Langmuir adsorption capacity ( $q_0$ ) (mg/g)	Freundlich coefficient ( $n$ )	References
Phosphate			
Nanostructured Fe-Al-Mn trimetal oxide	51.3–62.98	4.34–5.56	[19]
Fe-Mn binary oxide	58.78–123.66	7.94–16.13	[18]
Fe-Mn binary oxide nanoparticles	252–313	2.4–2.6	[17]
Laterite from Hubei, China	0.93–1.14	6.09–7.4	[49]
Ferric-modified laterites from Guangdong, China	21.01–31.53	2.68–3.1	[34]
Granular laterite from China	0.572	1.635	[50]
Industrial acidified laterite	2.73	0.07	[33]
Mn-doped Laterite from Thach That province, Northern Vietnam	22.22–31.25	3.17–3.24	This study
Fluoride			
Hydrous manganese oxide-coated alumina	7.09	10	[51]
Manganese oxide-coated graphene oxide	1.43–11.93	1.35–1.67	[52]
Zr-Mn composite material	3.05	14.5	[53]
Chemical-treated laterite from Kharagpur, India	32.28–41.01	0.33–0.38	[36]
Laterite from Ghana	0.55	18.19–40.00	[54]
Laterite from Bankura, India	0.60–0.86	1.69–2.33	[35]
Mn doped Laterite from Thach That province, Northern Vietnam	5.08–10.99	1.73–1.93	This study

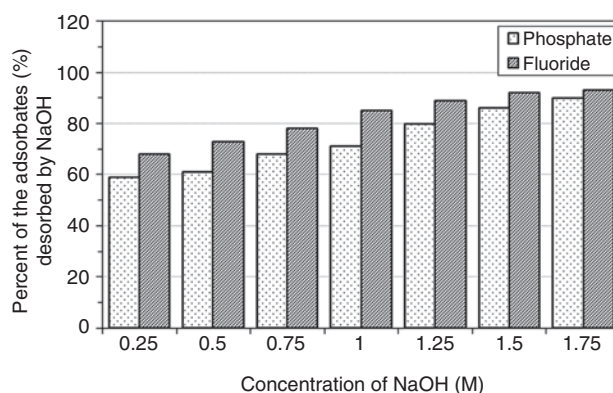
### 3.10 Influence of co-existing ions in water on the surveyed ion adsorption capacity of the material

In this study, the individual effects of co-existing ions (sulfate, chloride, nitrate), usually existing in industrial wastewater, were investigated. The initial concentration of the phosphate and fluoride was maintained at approximately 10 mg/l and 5 mg/l, respectively, while the concentrations (25–100 mg/l) of sulfate, chloride, and nitrate were varied in the adsorption studies. The initial pH and temperature of the solution was maintained at 6.5. It can be seen that the adsorptions of both fluoride and phosphate decrease with an increase in the co-ion concentrations (Supplemental Figure S4A, B). At 0 mg/l of the co-ions, phosphate and fluoride adsorbed 94.1% and 93.2%, respectively. However, the adsorption of phosphate and fluoride rapidly reduced to approximately 30% and 25% at 100 mg/l of co-ions. The decrease in the fluoride/phosphate uptake (Supplemental Figure S4A, B) may be caused by the competition between fluoride/phosphate and the co-ions, for the active sites on the surface of the adsorbent. The activity of the competing anions toward adsorption against adsorbates is in the following order:  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ . The reduction in the fluoride/phosphate removal in the presence of the sulfate ion may be attributed to the fact that the sulfate ion may have competition with the adsorbates for the same sorption sites, as the former forms a partial inner sphere complex-forming species [55] and the presence of the sulfate ion, being divalent, may

have increased the coulombic repulsive forces leading to the reduced probability of both fluoride and phosphate interactions with the active sites.

### 3.11 Regeneration MDL by NaOH

Any sorbent has an economical value, if it can be regenerated and reused in many cycles of operation. To study the reusability of the MDL, the adsorption studies were performed. After the complete saturation of the adsorbent, it was regenerated using NaOH solutions of concentrations ranging from 0.25 to 1.75 M. Figure 10 shows the percentage of desorption of the adsorbates obtained at various concentrations of the hydroxide solution. In 1.75 M of NaOH,

**Figure 10:** Influence of NaOH concentration for desorbing phosphate and fluoride from DML.

MDL desorbed almost 93% of the adsorbed fluoride and 90% of the adsorbed phosphate.

### 3.12 Experimental treatment of wastewater from the superphosphate fertilizer factory

Wastewater samples were taken from the waste channel of the Superphosphate Fertilizer factory, before it pours into the river. The phosphate and fluoride concentrations in the wastewater were detected to be 13.72 mg/l and 4.68 mg/l, respectively (data is shown in Supplemental Table S1).

The experimental treatment was carried out with an MDL-packed column having a diameter of 25 mm and a height of 200 mm. Material grain size was in the range of 0.1–0.5 mm. The flow rate was around 2.5 ml/min/cm<sup>2</sup>. The concentrations of the surveyed anions in effluent fractions were analyzed, and the results are described in Supplemental Figure S5.

The fluoride concentration did not appear in the first effluent fraction and quickly increased in the next ones. However, until the 12th fraction, its concentration (5–10 mg/l) was still lower than the allowable limit, level A of Vietnamese standards (QCVN 40:2011/BTNMT) for wastewater discharged to the environment. In the same way, the phosphate concentration was determined in the second fraction, and in 11th fraction, its concentration was also accepted for the wastewater discharge. Each fraction of 5000 ml was taken, and the tested column of 55,000–60,000 ml was completely treated for the wastewater to meet the allowable limit.

## 4 Conclusion

Manganese-doped laterite for simultaneous adsorption of phosphate and fluoride was successfully synthesized by the co-precipitation method. The fresh laterite layer, modified by manganese, has a high adsorption capacity with respect to phosphate and fluoride. When the manganese portion in this layer increases, the adsorbability also increases for both phosphate and fluoride. Besides, the adsorption capacity of the material was dependent on pH, contact time, and adsorbent dose. The optimum pH of 6 for the adsorption is close to the neutral region (5–7). In addition, the adsorption process of MDL followed the Langmuir and Freundlich isotherms. Furthermore, the influence of the concentrations of the co-existing

ions also decreases the adsorption capacity of MDL. The experimental treatment was carried out for the wastewater taken from the Superphosphate Fertilizer factory, and the results show that fresh manganese-based modified laterite is of low cost and is a good material for phosphate and fluoride treatment.

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## Bionotes



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