SYNTHESIS OF STARCH MODIFIED MONTMORILLONITE AS AN EFFECTIVE ADSORBENT FOR Pb (II) REMOVAL FROM WATER

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Abstract. The studied adsorbent was prepared by the starch modified montmorillonite for the removal of Pb (II) ions from aqueous solution. Fourier-transformed infrared (FTIR) spectroscopy and X-ray diffraction (XRD) were used to determine the structure and characteristics of the adsorbent. **M**ain factors affecting the removal of Pb (II) ions were investigated, including the pH, contact time, adsorbent dosage and the initial concentration of Pb (II). Batch process can be used for adsorption and equilibrium studies. The experimental data were fitted using Freundlich and Langmuir adsorption models. The Langmuir isotherm best fitted the experimental data with $R^2 > 0.99$ and maximum Pb (II) adsorption capacity of 21.5 mg/g indicating a monolayer adsorption type. Kinetic studies using pseudo-first-order and pseudo-second-order rate models showed that the process complied well with the pseudo second-order rate model.

Keywords: montmorillonite/starch, Pb (II) adsorption, starch.

Classification numbers: 3.4.2; 3.8.2.

1. INTRODUCTION

Water is one of the most valuable biospheric components and although it presents almost 70 % of the Earth's surface, only about 30 % is in the pure form, which is indispensable to the Earth life [1]. With the development of economy, environmental pollution occurs as a result of effluents released from the high toxicity of heavy metals such as lead, cadmium, mercury and

chromium, which is inimical to human health and the environment. In addition, this has become an increasing environmental concern in the develop countries [2, 3]. Because heavy metal contaminants are not biodegradable and decomposable, excessive amounts of them have extremely toxic effects to human, plants and animals. Lead can cause several diseases that affect the kidney, liver, nervous and reproductive systems, basic cellular processes and brain functions. This metal is widely used in batteries, mining, paints and pigments, ceramics, petroleum and weapon industries. Extreme exposure to Pb (II) levels above from 100 g/day may result in vertigo, migraine, insomnia, irritability, convulsions, seizures and coma [4]. The World Health Organization (WHO) recommended extremely low maximum acceptable concentration for cadmium, lead, nickel and chromium contamination in drinking water, which are 0.003 mg/L, 0.01 mg/L, 0.02 mg/L and 0.05 mg/L, respectively [5]. To solve the heavy metal contamination problem, various approaches including chemical precipitation, membrane separation, adsorption, electrolysis, coagulation, ion-exchange, and filtration, have been successfully applied to treat polluted water. Adsorption has been proved to be one of effective physical-chemical treatment methods for removing heavy metals from aqueous solution, thanks to the simple process and equipment. It has widely been applied on both industrial and natural water application because of its high efficiency, low-cost, easy operation and absence of contaminated byproducts [6-8]. The removal of heavy metals by adsorbents (cellulose, starch, chitin, chitosan, biomass etc.) has intensively been investigated. Recently, montmorillonite (MMT) is one the most abundant clay minerals (a natural material adsorbent) is a potent adsorbent that has been used to adsorb heavy metal ions from aqueous water and the physicochemical properties can be considerably modified by acid activation, soda activation, ion exchange, and heat treatments. However, it is noted that swelling can reduce the hydraulic conductivity of natural clay, so that the treated solution cannot seep into the clay easily. It is for this reason that natural clay cannot effectively adsorb metal ions from an aqueous solution [9, 10].

Starch has been receiving considerable attention and has been considered as one of the most promising candidates for the production of biodegradable materials because of its availability, relatively low cost, and renewable natural polysaccharide obtained from a great variety of crops [11].

In the present study, montmorillonite was intended to be modified by Vietnamese cassava starch for the use as adsorbent material to remove Pb (II) ions from aqueous solutions. The batch experiments have investigated process kinetics, effect of contributing parameters (pH, adsorbent dose, contact time, and initial metal concentration), and best fitting adsorption isotherm models (Langmuir and Freundlich).

2. MATERIALS AND METHODS

2.1. Reagents and materials

The montmorillonite (purity > 95 %) (MMT) was purified from raw bentonite in Lam Dong Province, Vietnam. Cassava starch (amylose pectin content > 80 % wt). Lead (II) nitrate was from Merck (Germany). A stock solution of (1000 mg/L) Pb salt in dilute nitric acid (2 %) was diluted quantitatively to prepare several aqueous solutions of desired concentrations (40 - 400 mg/L).

2.2. Experimental

2.2.1. Preparation of pure montmorillonite

10 gram of MMT from raw Bentonite in Lam Dong Province was added to 500 mL of distilled water and stirred for 24 hours. The mixture was transferred to a column (diameter of 15 cm and height of 1 m) for 12 hours. After settling, the bottom precipitation was removed and the obtained refined MMT was centrifuged at 7000 rpm and dried at 100°C for 8 hours.

2.2.2. Synthesis of the adsorbent

8 g of MMT was suspended in 500 mL of distilled water and then stirred for 48 hours. The starch was stirred in 100 mL of distilled water at 40°C for 30 mins. The starch solution was then added in MMT suspension with the containing 1.0 g of MMT and 0.6 g of Starch, and the sample was continuously stirred at room temperature during the next 4 hours. The modified MMT (MMT/starch) was collected by centrifugation at 7000 rpm and washed three times with distilled water. The sample was finally dried at 80 ^{o}C for 24 hours and sieved to obtain the particle size of below 200 μm. The result was studied by Advance D8 X-ray diffractometer (the radiation wavelength of the x-ray diffraction is 0.154 nm), which was used in the diffraction angle $2\theta = 2\text{-}20^{o}$ and a scanned speed of 0.1^{o}/s. The adsorbent was stored in a desiccator for the removal of Pb (II) ions from aqueous solutions in the next study.

2.3. Adsorption experiments

A measured amount of MMT/Starch (0.2 - 1.2 g) was carried out by immersing the adsorbent into 50 ml Pb (II) solution at pH of 4 to 6 and different initial concentrations (40 - 400 mg/L) under constant agitation. All adsorption experiments were examined through a batch method on a shaker with a constant speed at 150 rpm, the sample was centrifuged at 9000 rpm for 10 min and was removed of the adsorbent beads. The remaining Pb (II) was detected by an Inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer, Optima 8300). The adsorption capacities at any time (q_t, mg/g) and at equilibrium (q_e, mg/g) were calculated for each experiment using the following equations:

$$q_t = (C_o - C_t) * (V / m) \tag{1}$$

$$q_e = (C_o - C_e) * (V / m) \tag{2}$$

where C_o represents the initial lead ions concentration (mg/L), C_t is the remaining lead ions concentration in the solution at time t (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of the Pb (II) solution used for adsorption (L), and m is the weight of the dry adsorbent used (g). The removal percentage of Pb (II) ion was calculated according to the following equation:

$$R (\%) = (C_o - C_t) * (100 / C_o) \tag{3}$$

All reported experimental data are an average of two duplicate experiments. Pseudo first-order kinetic and pseudo second-order kinetic models of Pb (II) adsorption process were investigated by using the 1.0 g of adsorbent at the 40 - 400 (mg/L) lead ion solution with different shaking periods from 1 to 120 min at pH = 5.

3. RESULTS AND DISCUSSION

3.1. **Characterization of MMT/Starch**

FTIR method was used to analyze the effect of the interaction between MMT and starch molecules with different position at a peak of stretching band at of 2930.27 cm^{-1} and a broad peak of 3303.67 cm^{-1}. According to the harmonic oscillator model, the peaks were associated with inter- and intra-molecular interaction in the adsorbent [11]. On the other hand, the spectra showed two peak bands at 1415.29 cm^{-1} and 997.78 cm^{-1} can be seen as the stretch vibration of C-O band in the functional groups of C-O-H and C-O-C in the starch, respectively due to the starch molecules loading into the MMT [12].
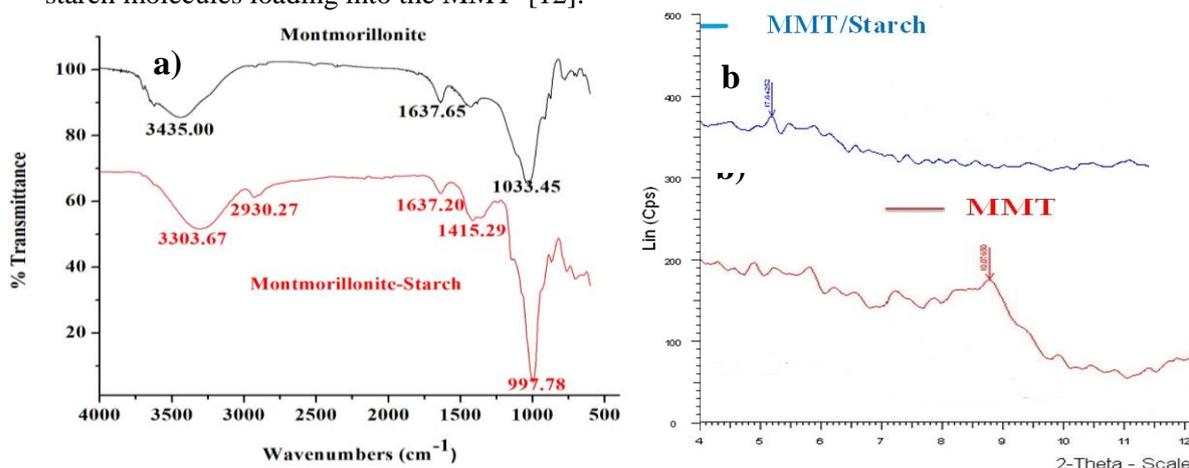

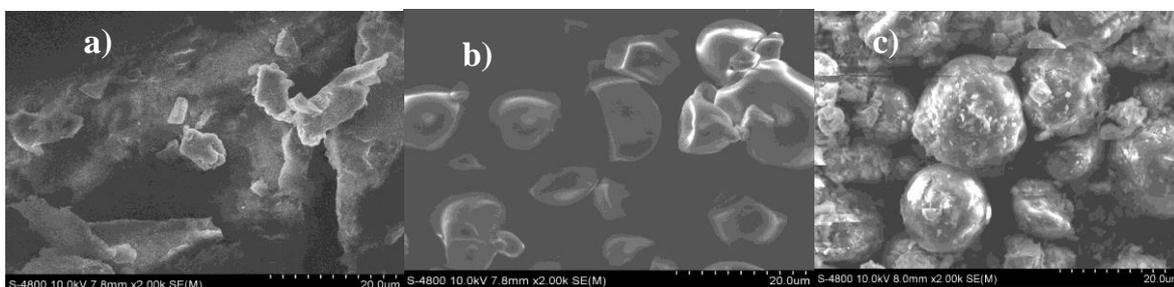*Figure 1.* FTIR spectra (a) and XRD pattern (b) of Montmorillonite and Montmorillonite-Starch.

Figure 2. SEM images of (a) MMT, b) Starch, (c) MMT/Starch adsorbent.

Scanning electron microscopy (SEM, S4800, Hitachi, Japan) images of MMT, Starch and MMT/Starch are shown in Fig. 2, the MMT and Starch particles exhibit a rugged surface and different size distribution with an average size of about 20 μm. Meanwhile, the surfaces of MMT/Starch particles have spherical shapes with clear geometric boundaries. Figure 1b indicated the XRD patterns obtained for the MMT, the MMT/Starch. The single 001 diffraction peak of MMT exhibited at 9° and the functional group was shifted to a lower angle at 5° from the original peak position [13]. Therefore, it can inferred that the loading Starch entered MMT and the MMT/Starch adsorbent was formed between MMT and Starch [14].

3.2. Influencing factors of Pb (II) adsorption

3.2.1. Influence of solution pH

The results, corresponding to the change of solution's pH values, are shown in Fig. 3a. The removal efficiency at a pH_o range of 4 - 6 increased slowly with the pH, when using 50 ml of lead ion solution (40 mg/L) and 1.0 g adsorbent for 1 h at room temperature. It could be due to the charge of the MMT/Starch and finally it affects ionic state of Pb (II) ion. In this study, we changed the pH of the lead ion solution from 4 to 6, this attraction between the Pb ions and MMT/Starch. However, the pH value increase in above 6 caused the formation of lead hydroxide (light white precipitate). Based on the adsorption capacity of Pb (II) ions, the pH value was controlled at pH = 5 which did not release the precipitate [8].

3.2.2. Effect of initial concentration

Figure 3b shows that the initial concentration (in the range from 10 to 40 mg/L) was investigated of the adsorption capacity of Pb (II) ions onto adsorbent that plays an important role in the understanding the removal adsorption behaviors.
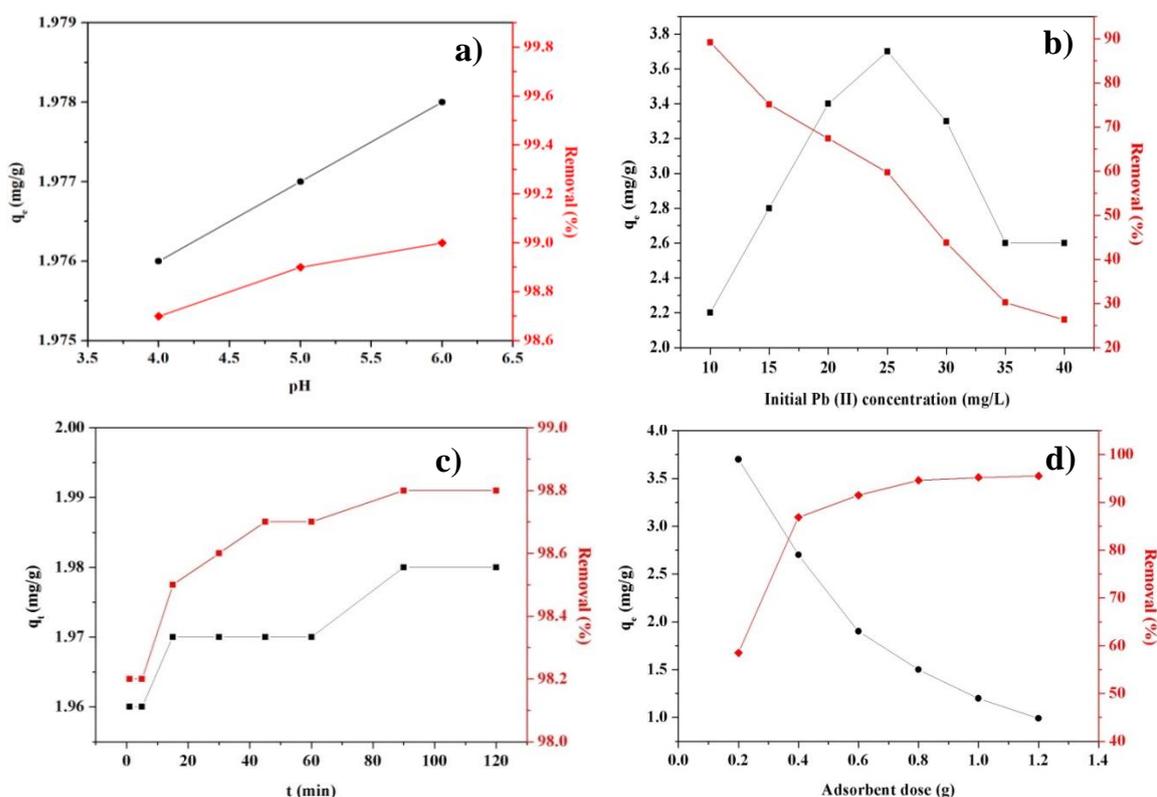

Figure 3. Influence of pH (a), initial concentration (b), contact time (c), and adsorbent dose (d) on the adsorption process of Pb (II) ions.

Amount of Pb (II) ion adsorbed per unit mass of Starch/MMT increased gradually with more and more Pb (II) ion in the adsorbate solution. At low Pb (II) ion loading, the ratio of the number of Pb (II) ion to the number of available adsorption sites is small and consequently, adsorption is independent of initial concentration, but as the Pb (II) ion increases, the situation change and the competition for adsorption sites becomes fierce. As a result, the extent of

adsorption comes down considerably, but the amount adsorbed per unit mass of the adsorbent rises [15].

3.2.3. Effect of adsorption time

Figure 3c describes that the effect of contact time (in the range from 1 min to 120 mins) on the adsorption capacity of Pb (II) solution was investigated to reach equilibrium. The removal efficiency was occurred sharply in the first minutes, reaching an equilibrium state after 90 min, and the removal capacity was above 98 % at 25 ^{o}C.

3.2.4. Effect of MMT/Starch dose

Figure 3d shows that the effect of the uptake capacity increases on adsorbent dosage (in the range from 0.2 g to 1.2 g). Therefore, the presence of more active sites on the adsorbent increasing the Pb (II) removal rate from aqueous solution and the accumulation of adsorbent may occur an excess of MMT/Starch reaching a saturated adsorption process, thus decrease to the utilizing rate of the adsorbent. In fact, the best adsorption capacity to remove Pb (II) ions on the adsorbent such as 1.0 g of adsorbent dosage was fitted all the experimental adsorption batches.

3.2.5. Adsorption kinetics

In order to understand the mechanism included in the controlling the adsorption process of Pb (II) ions onto MMT/Starch from aqueous solutions and thereby the pseudo first-order and pseudo second-order kinetic model obtain the valuable data for applying to analyze the experimental data. The two popular kinetic equations are given respectively.

Pseudo first-order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

Pseudo second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where k_1 and k_2 are the pseudo-first-order (min^{-1}) and pseudo-second-order (gmg^{-1}min^{-1}) rate, respectively; q_t and q_e are the amount of Pb (II) ions adsorbed on MMT/Starch at time t and at equilibrium (min). On the other hand, the linear plots of $\log(q_e - q_t)$ against (t) for the pseudo-first-order kinetic model and t/q_t against (t) for the pseudo second-order kinetic model are investigated to analyze the adsorption process, respectively.

Figure 4 (a,b) show the correlation coefficient (R^2) for the pseudo-second order model is closer to 1 ($R^2 > 0.99$) and is higher than that of the pseudo first-order kinetic model. Therefore, it can be concluded that the mechanism for the pseudo second-order kinetic model can explain the best adsorption equation of MMT/Starch for Pb (II) ions from aqueous solutions, providing that is mainly controlled by chemical process.

3.2.6. Equilibrium adsorption isotherm

The Langmuir and Freundlich isotherm models are shown the interactions of chemical bonds are formed between the adsorbate and the adsorbent by occuring at adsorption sites. Equilibrium studies of the parameters of adsorption process can indicate a very important role for optimizing the adsorbent dosage and understanding underlying mechanism. The adsorption process of Pb (II) ions on MMT/Starch was given by using different initial Pb (II) concentration (40-400 mg/L) at room temperature (25 ^{o}C), the shaking speed of 150 rpm and pH = 5 (Fig. 4c).
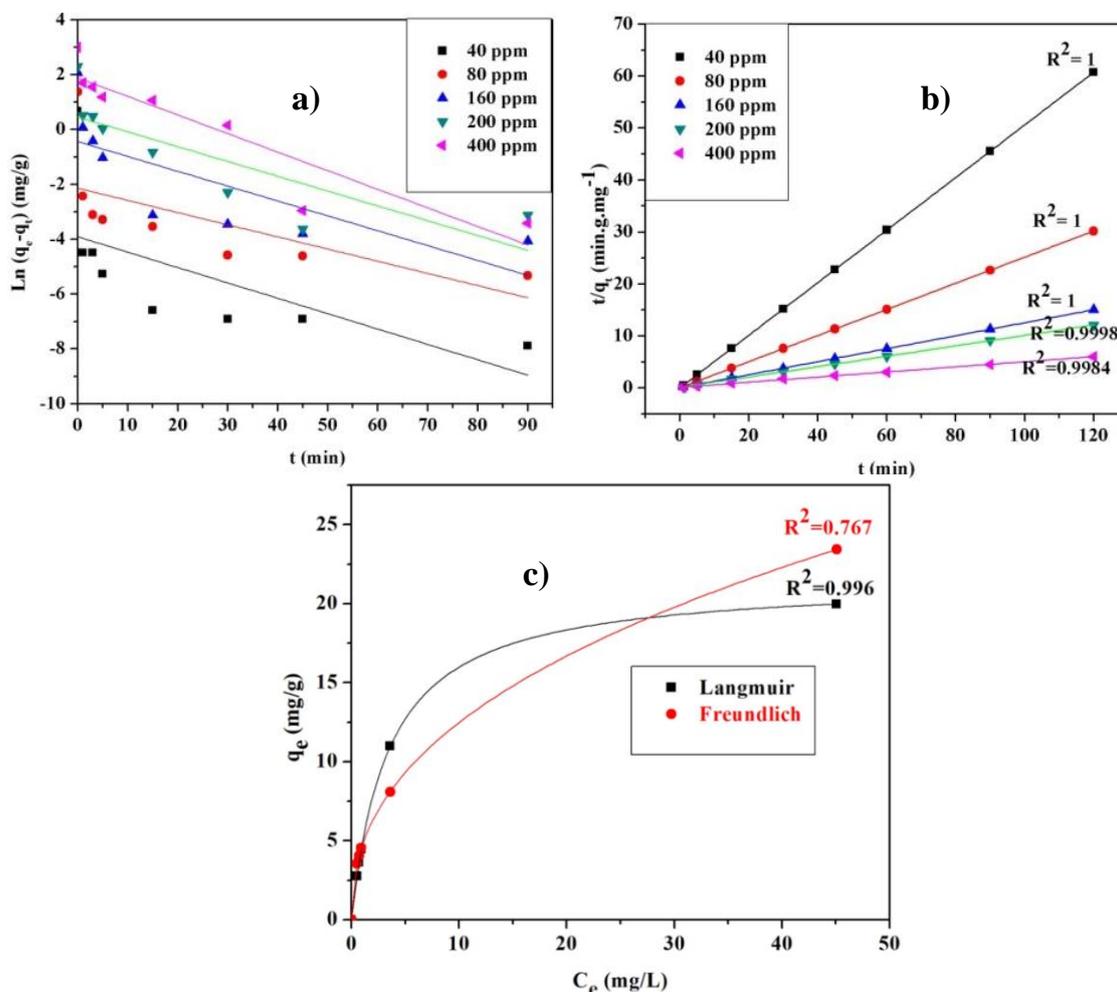

Figure 4. Adsorption kinetics data of Pb (II) ions onto MMT/Starch fitting to pseudo first-order (a), pseudo second-order kinetic models at initial concentrations (b), and Adsorption equilibrium data of Pb (II) ions on MMT/Starch from aqueous solution fitting to two isotherm equations (c).

The experimental data were fitted well with the high R^2 value (>0.99) (Table 1), and better for the Langmuir isotherm model than for the Freundlich isotherm model, indicating the homogeneous sites with monolayer adsorption of Pb (II) ions sorption onto MMT/Starch adsorbent. The adsorption isotherms are described by the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$ (6)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (7)$$

Table 1. Parameters of Langmuir and Freundlich models for the adsorption of Pb (II) ions on MMT/ Starch adsorbent.

Model		Parameters	
Isothermal models	Langmuir	b (L mg^{-1})	0.0074
		q_{max} (mg g^{-1})	21.5
		R^2	0.996
	Freundlich	K_F (mg g^{-1})	4.37
		n (L mg^{-1})	2.38
		R^2	0.767

where C_e (mg/L) and q_e (mg/g) describe respectively the Pb (II) concentration in solution and the adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption capacity; K_L and K_F (L/mg) are Langmuir and Freundlich adsorption equilibrium constants, respectively; n indicates heterogeneity factor related with the intensity of adsorption.

4. CONCLUSION

In the present study, a new adsorbent was prepared by incorporating Starch solution and MMT solution. Thereby, the structural properties were analyzed by the FTIR spectra and X-ray diffraction, which confirmed the existence of bonds of MMT/Starch in the synthesized material. The kinetic data of the adsorbent loading on Pb (II) ions could be well fitted in to the pseudo second-order model and the adsorption isotherm fits the Langmuir model with maximum uptake capacity of about 21.5 mg/g, which is lower than the MMT with the q_{max} value on the adsorption capacity (31.1 mg/g) reported by [15]. Furthermore, the experimental results indicate chemisorption as the rate controlling adsorption mechanism for Pb (II) ions on MMT/Starch.

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