

# Dextrin/MMT Nanocomposite Explored for the Removal of Pb(II) from Aqueous Solution

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**Abstract**—Nanotechnology is an alarming and emerging field in the area of environmental chemistry. Nanocomposite offers considerable attention owing to its chemical and physical properties for the removal of heavy metals from wastewater. Dextrin/Montmorillonite nanocomposite has been successfully synthesized and has been explored for the removal of Pb(II) from aqueous solution. The nanocomposite has been characterized using SEM, TEM and FTIR techniques. The adsorption of Pb(II) ions was dependent on the initial Pb(II) ion concentration, pH, temperature and contact time. The adsorption isotherm could be described by the Langmuir and Freundlich isotherm models. Freundlich was the best suited model for the adsorption of Pb(II) onto nanocomposite. Kinetic models-pseudo first and pseudo second order kinetic models were also evaluated. Kinetics was the best suited by pseudo second order kinetic model. Thermodynamic parameters such as  $\Delta H^0$ ,  $\Delta G^0$  and  $\Delta S^0$  were also calculated. The thermodynamic parameters shows that the process to be exothermic, spontaneous with increased randomness of the adsorbent. Therefore, the present potential and eco-friendly nanocomposite has been proved to be an excellent adsorbent that could be explored for the removal of toxic and carcinogenic heavy metals.

**Keywords:** Nanocomposite, Isotherms, Kinetics, Thermodynamics.

## 1. INTRODUCTION

Heavy metals are toxic and carcinogenic pollutants that badly affects human health and ecosystem due to their bioaccumulating, persisting, non-biodegradable nature[1]. Pb(II) is one of the most toxic and carcinogenic heavy metal that is being discharged from various industries such as textile dyeing, petroleum refining, tanneries etc. It causes various serious health issues effecting brain, lungs, cardiovascular system, kidney, muscle and other vital organs [2]. Adsorption is generally the preferred technique for the removal of heavy metals due to its ease in operation, insensitive to toxic substance, reusable nature, efficient and cost effective nature [3]. In the present study, biopolymer nanocomposite has been explored as an adsorbent for the removal of Pb(II) from aqueous solution. Biopolymer, Dextrin is a low molecular weight carbohydrates produced by hydrolysis of starch or glycogen [4].

Montmorillonite is a 2:1 type consisting of two tetrahedral sheets separated by an octahedral sheet with high chemical

stability, high sorption properties and rich intercalation chemistry [5].

In order to study the adsorption behavior of present nanocomposite, batch adsorption experiments were conducted such as influence of pH, contact time, concentration, temperature. Moreover, Kinetics, isotherms and thermodynamic studies were also included in the paper to analyze the adsorption process. Scanning electron microscope (SEM), Fourier transform Infrared spectroscopy (FTIR) and Transmission electron microscope (TEM) micrographs were also been included.

## 2. MATERIALS AND METHOD

### 2.1. Materials

Prior to use all glasswares were nicely washed and rinsed. Lead nitrate salt was purchased from Merck, India. Dextrin were obtained from CDH, New Delhi. Montmorillonite was purchased from Sigma-Aldrich (USA). Stock solution (1000 mgL<sup>-1</sup>) of Pb(II) was prepared by dissolving requisite amount of lead nitrate salt in double distilled water. All other chemicals used were of analytical grade. Double distilled water was used throughout the experiment.

### 2.2. Synthesis of nanocomposite

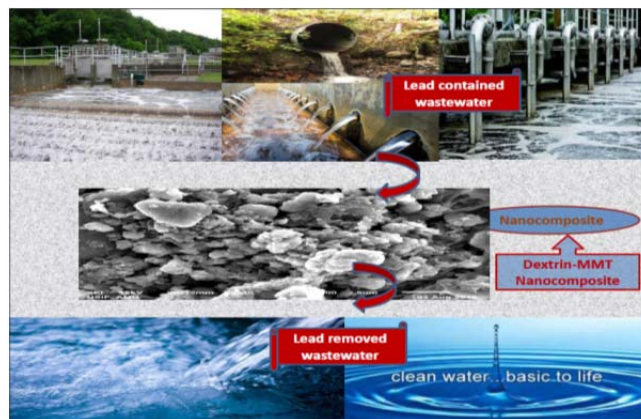


Fig. 1: Graphical representation of Pb(II) removal by nanocomposite.

6 g of montmorillonite was left for dispersion (400 rpm) in 150 mL of water for 24 h at 60 °C. 6 g of dextrin was dissolved in 150 mL of water. To this solution, montmorillonite solution was added slowly with continuous stirring at 600 rpm at 60 °C for 24 h. The solution was precipitated using 200 mL acetone. Filter, washed, dried and powdered the nanocomposite in mortar for subsequent studies.

### 3. CHARACTERIZATION

SEM images were observed before and after adsorption onto nanocomposite using SEM (model JSM 6510 LV, JEOL, Japan). The sample were mounted on a copper stub and then coated with gold .The particle size of nanocomposite was analyzed using TEM (JEM 2100, JEOL, Japan) placed on carbon coated copper grid. FTIR spectra were obtained on a FTIR spectrophotometer in the wavenumber ranging from 400-4000  $\text{cm}^{-1}$  using KBr discs (Nicolet iS50 FT-IR). The concentration of metal ions were detected using Atomic absorption spectrophotometer (GBC 902, Australia).

### 4. BATCH ADSORPTION EXPERIMENT

The influence of various important parameters such as pH (1-7), contact time (5-360 min), initial concentration (10-100  $\text{mgL}^{-1}$ ) and temperature (298-318 K) were analyzed using batch adsorption mode. Influence of pH (1-7) was analyzed by treating the nanocomposite (0.02 g) in Pb(II) solution of concentration (50  $\text{mgL}^{-1}$ , 20 mL) for 24 h at room temperature (298K). 0.5 M HCl and 0.5 M NaOH were used to adjust the pH. Influence of contact time (5-360 min) was analyzed by treating the nanocomposite (0.02 g) in Pb(II) solution of concentration (50  $\text{mgL}^{-1}$ , 20 mL) at room temperature (298K) and pH 5 for variable time intervals. Influence of concentration was analyzed by treating the nanocomposite (0.02 g) in Pb(II) solution of concentration (10-100  $\text{mgL}^{-1}$ , 20 mL, pH 5) for 120 min at room temperature (298K) at 110 rpm. The temperature effect was analyzed by treating the nanocomposite (0.02 g) in Pb(II) solution of concentration (50  $\text{mgL}^{-1}$ , 20 mL, pH 5) for 120 min at temperature range (298-318K) at 110 rpm. The removal efficiency (%) and adsorption capacity ( $q_e$ ) ( $\text{mgg}^{-1}$ ) of Pb(II) onto nanocomposite were calculated using “(1) and (2)” as follows:

$$\% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

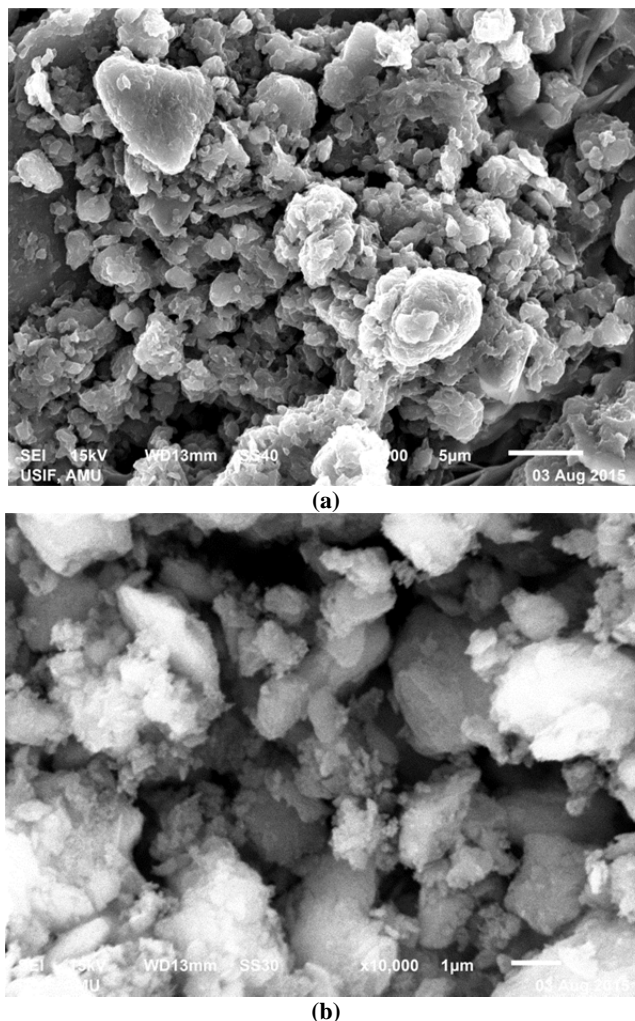
$$q_e = \frac{C_o - C_e}{W} \times V \quad (2)$$

Where,  $C_o$  and  $C_e$  are the initial and equilibrium concentration of Pb(II) ( $\text{mgL}^{-1}$ ),  $V$  (L) is the volume of Pb(II) ion solution used and  $W$  is the mass of nanocomposite used (g) [6].

## 5. RESULTS AND DISCUSSION

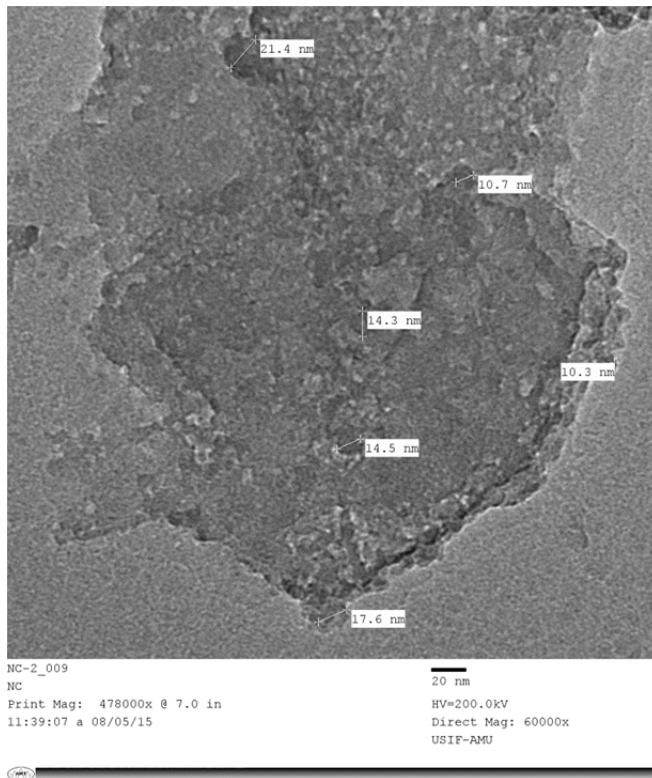
### 5.1. Characterization

SEM micrographs of nanocomposite were shown in Fig. 2 (a) and Pb(II) loaded nanocomposite in Fig. 2 (b).



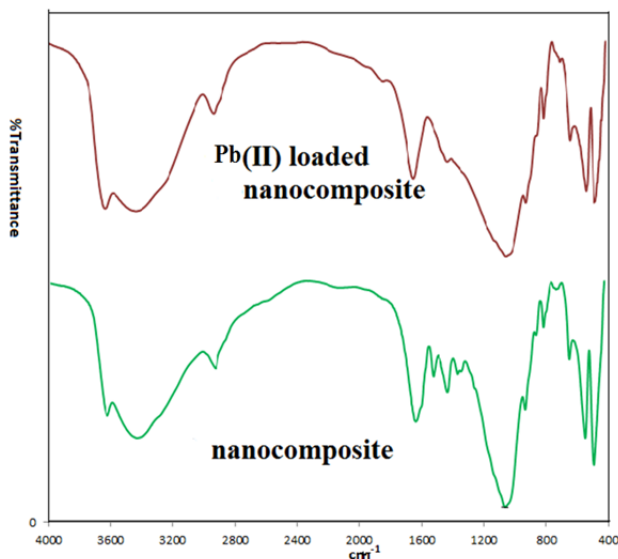
**Fig. 2: SEM micrographs (10,000X) of (a) nanocomposite (b) Pb(II) loaded nanocomposite.**

The Fig. 2 (a) shows the heterogenous and porous surface of nanocomposite and Fig. 2 (b) shows the smooth surface that showed the adsorption of Pb(II) onto the surface of nanocomposite. TEM image of nanocomposite (Fig. 3) shows particle being dispersed throughout the surface and the size ranges in approximately 7-27 nm.



**Fig. 3: TEM image of nanocomposite.**

The FTIR spectra of nanocomposite and Pb(II) loaded nanocomposite were shown in Fig. 4.



**Fig. 4: FTIR spectra**

The peaks of nanocomposite were observed at 3636, 3446, 2929, 1637, 1042 and 471 cm<sup>-1</sup>, respectively. The peaks corresponds to the presence of OH stretching, CH<sub>2</sub> stretching, C=O stretching, C-O stretching and Si-O-Si stretching, respectively. There is shift in peaks in Pb(II) loaded

nanocomposite that showed the successful loading of Pb(II) onto nanocomposite.

## 5.2. Batch adsorption experiments

### 5.2.1. Effect of pH

With increase in pH from 1 to 5, the adsorption capacity increases (31 to 52 mgg<sup>-1</sup>) and reaches maximum at pH 5 (52 mgg<sup>-1</sup>) and from pH (6 to 7) the adsorption capacity starts decreasing (51 to 50 mgg<sup>-1</sup>). This trend could be explained as follows: At lower pH, there is predominance of H<sup>+</sup> that competes with Pb(II) and as the pH increases the population of H<sup>+</sup> starts decreasing and surface become more negatively charged and there is predominance of Pb(II) that enhances its adsorption on the vacant sites of nanocomposite [6].

### 5.2.2. Effect of contact time and adsorption kinetics

With increase in time interval from 5 to 120 min, the adsorption capacity increases from 15 to 57 mgg<sup>-1</sup> with maximum adsorption occur at 120 min (57 mgg<sup>-1</sup>) and from 120-360 min, there is saturation in adsorption capacity (43.48 mgg<sup>-1</sup>). This could be explained as follows: The initial rapid uptake of metal ion is due to the maximum availability of active sites that gradually decreases after 120 min and hence, there is downfall in adsorption capacity after 120 min [7]. To understand the adsorption kinetics and rate of adsorption, pseudo-first order “(3)” and pseudo-second order “(4)” kinetic models were employed as follows:

$$qt = qe(1 - e^{-k_1t}) \quad (3)$$

$$qt = \frac{k_2qe^2t}{1 + k_2qet} \quad (4)$$

Where,  $q_{e-cal}$  or  $q_e$  (mgg<sup>-1</sup>) is the calculated equilibrium adsorption capacity, and  $q_{e-exp}$  (mgg<sup>-1</sup>) is the experimental equilibrium adsorption capacity.  $K_1$  (min<sup>-1</sup>) and  $K_2$  (gmg<sup>-1</sup> min<sup>-1</sup>) are the pseudo-first order and pseudo-second order rate constant respectively [8].

The parameters of models were tabulated in Table 1. Pseudo-second order showed better fitted kinetic model as compared to pseudo-first order in accordance of high correlation coefficient value ( $R^2$ ) and also, the value of  $q_{e-exp}$  and  $q_{e-cal}$  were close to each other (Fig. 5). This indicates that chemisorption is the rate-determining step in the adsorption process [6].

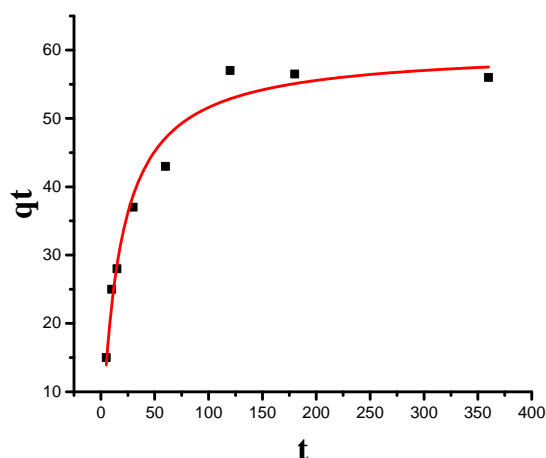


Fig. 5: Pseudo-second order kinetic model (condition: pH 5, conc. 50 mgL<sup>-1</sup>, temperature 298K, dose 0.02 g).

Table 1: Model parameters

Kinetic parameters	Isotherm parameters
Pseudo-first order	Langmuir
qe-exp (mgg <sup>-1</sup> ) 58	qm (mgg <sup>-1</sup> ) 284.593
qe-cal (mgg <sup>-1</sup> ) 54.313	b (Lmg <sup>-1</sup> ) 0.01241
k <sub>1</sub> (min <sup>-1</sup> ) 0.0457	R <sup>2</sup> 0.97818
R <sup>2</sup> 0.9159	
Pseudo-second order	Freundlich
qe-exp (mgg <sup>-1</sup> ) 58	K <sub>F</sub> (mgg <sup>-1</sup> )(Lmg <sup>-1</sup> ) <sup>(1/n)</sup> 4.1396
qe-cal (mgg <sup>-1</sup> ) 60.174	n 1.1406
k <sub>2</sub> (gm <sup>-1</sup> min <sup>-1</sup> ) 0.001	R <sup>2</sup> 0.9835
R <sup>2</sup> 0.968	

### 5.2.3. Effect of concentration and adsorption isotherms

With increase in concentration from 10 to 100 mgL<sup>-1</sup>, the adsorption capacity increases (8.2 to 50 mgg<sup>-1</sup>). This fact might be due to the increased concentration gradient between bulk solution and nanocomposite. To understand the relationship between the adsorbate and adsorbent, various non-linear adsorption isotherm were employed namely, Langmuir “(5)” and Freundlich “(6)” isotherm models respectively as follows:

$$qe = \frac{qmbCe}{1+bCe} \quad (5)$$

$$qe = K_F Ce^{1/n} \quad (6)$$

Where, qm is the monolayer adsorption capacity (mgg<sup>-1</sup>), b is the Langmuir constant (Lmg<sup>-1</sup>), K<sub>F</sub> is a constant related to adsorption capacity (mgg<sup>-1</sup>)(Lmg<sup>-1</sup>)<sup>(1/n)</sup> and n signifies the adsorption intensity of adsorbent [8]. The model parameters were tabulated in Table 1. In synchronization with the Table 1, it was found that the Freundlich is the best obeyed isotherm model indicating heterogenous nature of adsorbent and as the value of n>1, indicating favourable adsorption (Fig. 6) [6], [7].

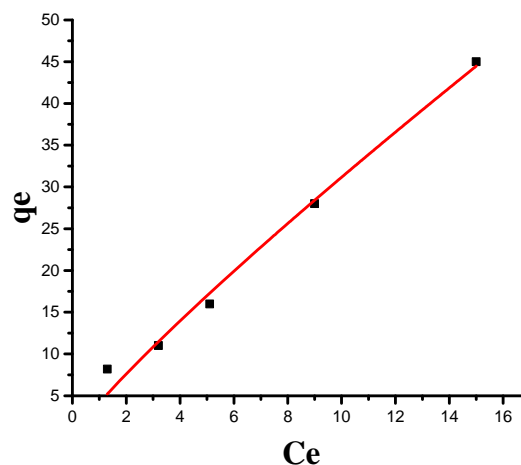


Fig. 6: Freundlich isotherm model (condition: pH 5, contact time 120 min, temperature 298K, dose 0.02 g).

### 5.2.4. Effect of temperature and Thermodynamic study

It was found that adsorption capacity decreases (43.57 to 41.86 mgg<sup>-1</sup>) with increase in temperature (298-318 K) suggesting exothermic nature of adsorption. Various thermodynamic parameters such as change in enthalpy ( $\Delta H$ , kJmol<sup>-1</sup>), Change in Gibbs free energy ( $\Delta G$ , kJmol<sup>-1</sup>) and change in entropy ( $\Delta S$ , kJmol<sup>-1</sup>K<sup>-1</sup>) were calculated using “(7, 8)”:

$$\Delta G = -RT \ln Kc \quad (7)$$

$$\log Kc = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (8)$$

Where, Kc is the equilibrium constant, T is the temperature (K), R is the universal gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>) (Fig. 7) [6], [9].

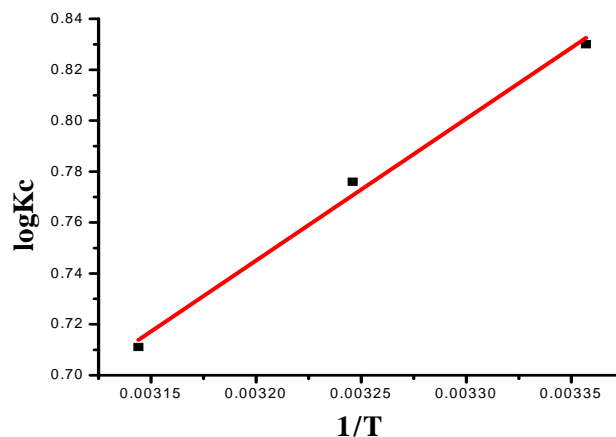


Fig. 7 logKc v/s 1/T (condition: conc 50 mgL<sup>-1</sup>, pH 5, dose 0.02 g, contact time 120 min).

The value of  $\Delta H$  and  $\Delta S$  were  $-10.668 \text{ kJmol}^{-1}$  and  $0.0198 \text{ kJmol}^{-1}$  respectively signifying exothermic nature of adsorption and increased randomness at solid/liquid interface during the adsorption of Pb(II) onto nanocomposite. The values of  $\Delta G$  at temperature 298, 308 and 318K were found to be  $-4.740$ ,  $-4.580$  and  $-4.329 \text{ kJmol}^{-1}$  respectively indicating spontaneous nature of adsorption and physiosorption process of adsorption [6], [9].

## 6. CONCLUSION

Based on proposed research, we conclude that:

A novel ecofriendly nanocomposite has been explored for the excellent removal of toxic Pb(II) from artificially prepared aqueous solution of Pb(II). The SEM shows heterogenous nature of adsorption and Pb(II) loaded nanocomposite shows successful loading of nanocomposite. TEM of nanocomposite shows the size of particles lies in the range of 7-27 nm. Various batch adsorption experiments were conducted in order to get the optimum conditions for adsorption process. The maximum adsorption were found to be at pH 5 ( $52 \text{ mgg}^{-1}$ ), temperature 298K ( $43.57 \text{ mgg}^{-1}$ ), contact time 120 min ( $57 \text{ mgg}^{-1}$ ) and concentration  $100 \text{ mgL}^{-1}$  ( $50 \text{ mgg}^{-1}$ ). Freundlich isotherm was the best obeyed model suggesting heterogenous nanocomposite surface. Langmuir monolayer adsorption capacity was found to be  $284.593 \text{ mgg}^{-1}$ . Pseudo second order is the best fitted kinetic model suggesting chemisorption as rate determining step. Thermodynamic studies shows spontaneous, exothermic adsorption process and increased randomness at solid/liquid interface. Chemical and physical adsorption process were involved in successful removal of Pb(II) via present nanocomposite. The study highlights the potential use of present promising and novel nanocomposite for the effective sequestration of toxic metals from aqueous solution and this nanocomposite could be explored for heavy metals removal from wastewater.

## 7. ACKNOWLEDGMENTS

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