

Adsorption of Pb(II) from aqueous solution using MCM-41: Kinetic Studies

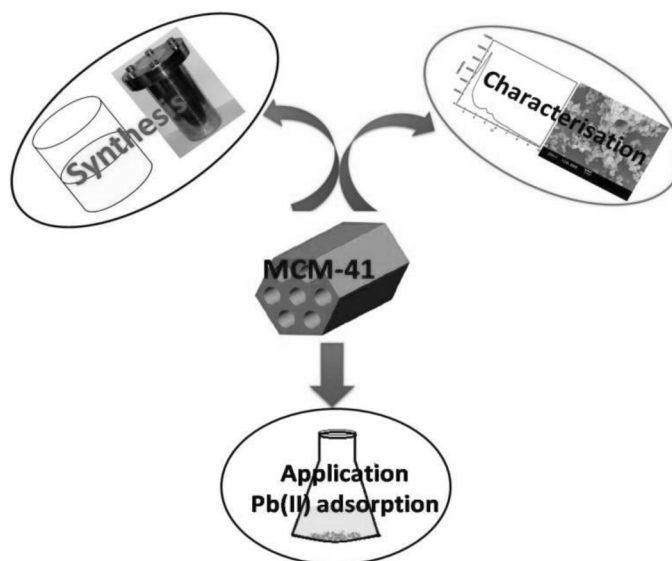
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ABSTRACT

The present work deals with the adsorption of Pb(II) on mesoporous MCM-41. Characterization of the adsorbent was done using XRD, TGA, FTIR and SEM. The batch method was employed to study the influential parameters such as contact time, adsorbent dose and initial metal ion concentration with an agitation speed of 220 rpm. Pb(II) removal increased with increasing contact time at different initial concentration. The removal of Pb(II) was found to be approximately 90.54% with 0.2 g of the same adsorbent with 74 mg/L Pb(II) concentration. The study on the effect of initial metal ion concentration disclosed that the adsorption capacity was increased to approximately 99.9% at low initial Pb(II) ion concentration 24 mg/L. The adsorption process was found to follow pseudo second-order kinetic model as revealed from the kinetic models studied. The results showed that MCM-41 could be considered as a potential adsorbent for the removal of Pb(II) from aqueous solution.



Key Words: MCM-41, adsorption, lead, adsorption kinetics

INTRODUCTION

The increasing level of toxic metals that are discharged to the environment as industrial waste has been proved to be a serious threat to human health, living resources and ecological system. Studies of contaminant sorption onto soils and natural sediments and transport of contaminants in surface and ground water have drawn great interest in the recent years. Many heavy toxic metals, particularly Pb^{+2} , Cr^{+3} , Fe^{+3} and Cu^{+2} tend to accumulate in organism causing numerous diseases and disorders [1, 2]. There are many sources of heavy metals, specifically mining wastes and acid mine drainage contribute significant quantities of dissolved metals to effluent streams. Other sources are fertilizer manufacturing, petroleum refining, paints and pigments, steel works, foundries, electroplating and electrical equipment, brass etc. Lead among the heavy metal ions in excess quantities in human body cause very serious health problems. Lead interferes with a number of body functions and affects heart, bones, kidneys, central nervous, hematopoietic, hepatic and renal systems, producing serious disorders [3,4]. It is therefore essential to remove these heavy metal ions from industrial effluents before discharging into the water resources.

Several methods like chemical precipitation, reverse osmosis, solvent extraction, phytoextraction, ion exchange, ultra filtration, electrodialysis and adsorption are available for the removal of metal ions from contaminated water [5-8]. Out of these methods, adsorption appears to be most effective and widely used technique for the removal of toxic heavy metals from waste water. The most widely used adsorbent for this purpose is activated carbon, silica and zeolites [9,10].

One of the most exciting discoveries in the field of material engineering is the synthesis of a new family of mesoporous siliceous materials designated as M41S with exceptionally large and uniform pores by Mobil Oil Corporation Research group in 1992 [11,12]. Large uniform pore sizes (2-50 nm), highly ordered nanochannels, large surface

areas (up to $1500 \text{ m}^2/\text{g}$) and attractive liquid crystal structures are the desirable properties which make these materials the focus of great interest. Typical mesoporous materials include some kinds of silica and alumina that have similarly sized fine mesopores. The discovery of these materials has greatly enlarged the window of porous materials for industrial applications [13-15]. Taking into account numerous sources of heavy metal contamination, the overall focus of this study was to ascertain the adsorption performance of the mesoporous material MCM-41 for Pb(II) from aqueous solution.

MATERIAL AND METHODS

Materials

All the chemicals such as cetyltrimethylammoniumbromide (CTAB, RANKEM), tetraethylorthosilicate (TEOS, Merck), ammonium hydroxide (25%), absolute alcohol, $\text{Pb}(\text{NO}_3)_2$ were of analytical grade and used as received without further purification. De-ionized water was used throughout this study for solution preparation and washing.

Synthesis of MCM-41

MCM-41 was synthesized with a procedure similar to that in the literature [16] in one step and double solvent medium in a short period of time. In a typical synthesis procedure, CTAB was dissolved in a mixture of water and ethanol. Ammonia solution and sodium acetate were added to the mixture. After about 10 min stirring when a clear solution was obtained, silica source was added at one time. The final molar composition of the resulting gel was TEOS:1 ; CTAB:0.22; sodium acetate:0.034; NH_3 :11; ethanol:1; water:155. After 2.5 h stirring at room temperature the obtained gel was then transferred to a Teflon-lined stainless steel autoclave and heated at 343 K for 5 h. The product was recovered by filtration, washed with distilled water and then dried at room temperature. Calcination was carried out in air at a heating rate of 1K/min upto 823 K and held at this temperature for 5 h.

Characterisation

The synthesized material was characterised by X-ray diffraction (XRD), thermogravimetric analysis (TGA), fourier

transform infrared (FTIR) spectroscopy and Scanning Electron microscopy (SEM) analysis. XRD analysis of the samples was

carried out on a Bruker D8 advance instrument operating at 40 kV and 40 mA using Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$). The diffraction data were recorded in the 2θ range of $2-10^\circ$. FTIR spectra were recorded on IR Affinity-1 Fourier transform infrared spectrophotometer (SHIMADZU) instrument in transmittance mode in KBr in the range of $4000-450 \text{ cm}^{-1}$. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC1 STAR^c System. The thermal investigation was carried out under a nitrogen atmosphere by heating the samples from $50^\circ-700^\circ\text{C}$ in a silica crucible at a heating rate of $10^\circ\text{C} / \text{min}$.

Batch adsorption experiment

Batch adsorption experiments were carried out by varying parameters such as contact time (5-180 min), adsorbent dosage (0.05-0.2 g) and initial concentration (24 -74 mg/L) using the adsorbent in 100 mL stoppered conical flasks containing 20 mL of the metal ion solutions of desired concentration. During the adsorption process, the flasks were agitated on a electrical shaker at a constant speed of 200 rpm at room temperature. The contents of the flasks were filtered through Whatman filter paper (No.41) and the filtrates were acidified with 2% HNO_3 to decrease the pH value below 3 in order to avoid any precipitation before the AAS measurement. The filtered samples were poured into plastic bottles and the exact

concentration of metal ions and filterable metal concentrations were determined by atomic absorption spectrophotometer (AAS). The adsorption percentage of Pb(II) was calculated as follows-

$$\% \text{ of adsorption} = \frac{C_i - C_f}{C_f} \times 100 \quad \text{-----}$$

- (1)

where C_i and C_f are the initial and final concentrations i.e. before and after adsorption of the metal ion in solution respectively.

RESULT AND DISCUSSION

Characterization of the adsorbent

In XRD pattern of MCM-41 (Fig.1) a sharp and intense peak at $2\theta= 2.4$ and two additional diffraction peaks at 2θ values 4.5 and 5.3 are observed being indicative of well-ordered hexagonal mesoporous structure. The thermal curve of uncalcined MCM-41 shows three distinct region of weight loss (Fig.2). The first weight loss at temperature below 150°C is attributed to the removal of physically adsorbed water on the external surface. Breaking of hydrocarbon chain present in the surfactant CTAB causes the second region of weight loss in the range of 200 to 550°C . The weight loss in the third region i.e. between 550 and 700°C is possibly due to decomposition of germinal and vicinal silanol groups present in the sample.

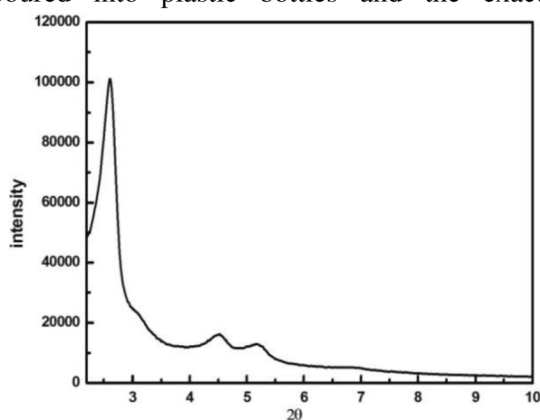


Fig.1 XRD analysis of MCM-41

The FT-IR spectra of MCM-41 is shown in Fig.3. The bands at around 1074 , 795 and 459 cm^{-1} were typical Si-O-Si (asymmetric stretching, symmetric stretching and bending) bands attributed to the condensed silica network. A broad adsorption band at around

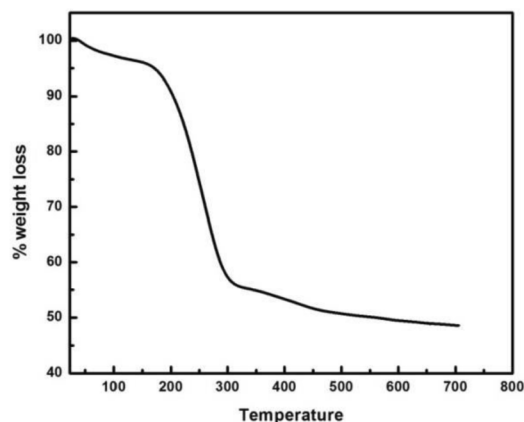


Fig. 2 TGA of uncalcined MCM-41

3500 cm^{-1} was assigned to O-H stretching. The absorption band around 1630 cm^{-1} was mainly due to bending vibration of adsorbed water. SEM image of MCM-41 (Fig.4) showed that the particles are spherical in shape with size $0.3-0.6 \mu\text{m}$.

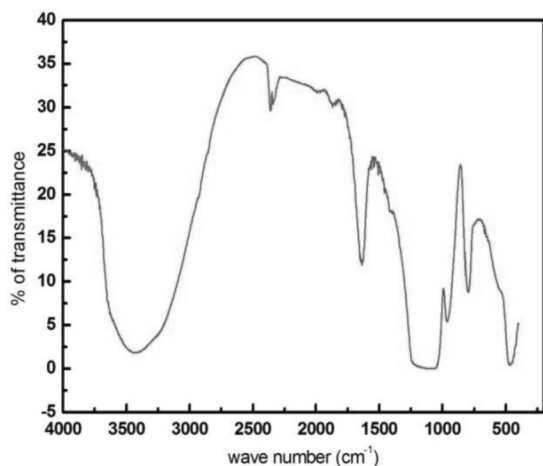


Fig.3 FTIR spectra of calcined MCM-41

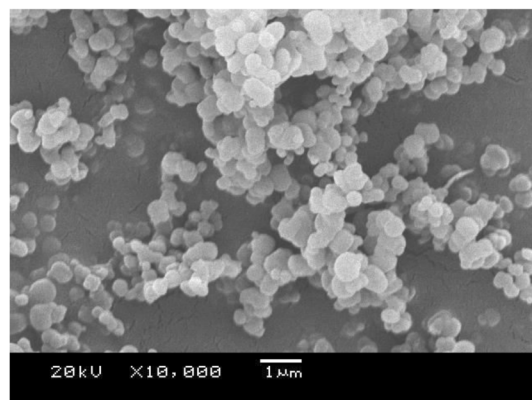


Fig. 4 SEM of calcined MCM-41

Batch adsorption experiment

Effect of adsorbent dose

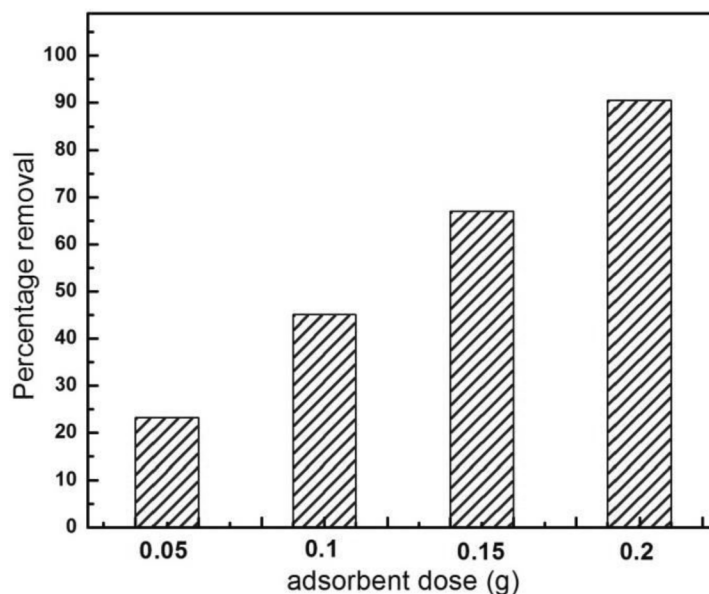


Fig. 5 Effect of adsorbent dose on adsorption of Pb(II) onto MCM-41 (contact time= 1h, initial

concentration = 74 mg/L)

The effect of adsorbent dose on percentage removal of Pb(II) onto MCM-41 is shown in Fig.5 for 1 h contact time. It was found that with increase in adsorbent doses from 0.05g to 0.2g percentage removal increased from 23.27 to 90.54% from Pb(II) solution of

concentration 74 mg/L. The increase in adsorption percentage can be attributed to the fact that with increasing the adsorbent dose, more adsorbent surface is available for the solute to be adsorbed and hence the availability of more adsorption sites.

Effect of contact time and initial concentration

Fig. 6 shows the effect of contact time (5-180 min) and initial metal ion concentration (24-74 mg/L) on removal of Pb(II) from aqueous solution. As seen from Fig.6 percentage removal of Pb(II) increased with increasing contact time. Rapid adsorption rate was observed during the first 60 min of contact time and slowed down gradually and reached an equilibrium within 60 min because the available adsorptive sites decreased as the

adsorption proceeded. It is also observed that percentage removal of Pb(II) on MCM-41 decreased from 99.9% to 63.5% as the initial Pb(II) concentration was increased from 24 to 74 mg/L. The lower adsorption capacity in high metal ion concentration was due to the limited available active sites for a fixed adsorbent dose which became saturated at a certain concentration.

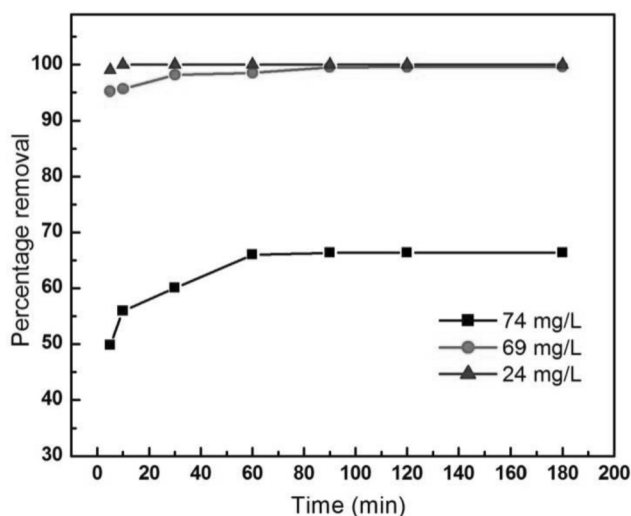


Fig. 6 Effect of contact time and initial concentration on Pb(II) adsorption (dose = 0.15 g)

Kinetic studies

In this study, pseudo-first order or Lagergren equation and pseudo-second order kinetic models were applied to find the best fitted model for the experimental data.

Pseudo-first-order kinetic model

The pseudo-first order or Lagergren equation is one of the most popular kinetic equation which is given as equation 2.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{-----2}$$

Where q_e and q_t are the amounts of solute adsorbed by the adsorbent (mg g^{-1}) at equilibrium and at time t . k_1 is the rate constant (min^{-1}) [17]. The q_e is calculated using equation 3:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad \text{----- 3}$$

Where C_0 is the initial solute concentration (mgL^{-1}), C_e is the equilibrium concentration

(mgL^{-1}), V is the volume of the solute solution (mL) and W is the weight of the adsorbent (g). By applying equation 2, the plot of $\log(q_e - q_t)$ vs t gives a straight line [Fig.7(a)] and the values of k_1 , $q_{e,\text{cal}}$ and the correlation coefficients R^2 obtained from the plots are presented in Table 2. The values of R^2 are found to be relatively small. It was also observed that the $q_{e,\text{cal}}$ values calculated from the Lagergren plots did not agree with the experimental q_e value i.e. $q_{e,\text{exp}}$ (Table 1). The equilibrium adsorption capacity, q_e , obtained from the plots deviated by 95.29% and 63.44% respectively from the experimental value. This indicated that the adsorption of Pb(II) on MCM-41 did not fit with the pseudo-first-order kinetics.

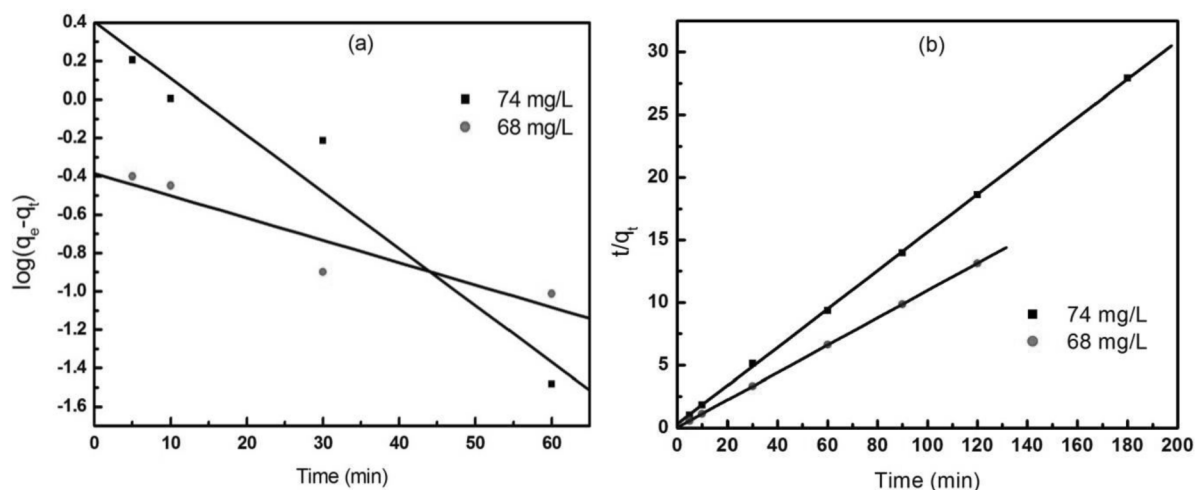


Fig. 7 Plot of different kinetic models, (a) pseudo-first order kinetic and (b) pseudo-second order kinetic

Table 1. Kinetic parameters for adsorption of Pb(II) on MCM-41

Metal	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order			Pseudo second order				
			$q_{e,cal}$ (mg/g)	Deviati on (%)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	Deviati on (%)	k_2 ($\text{mg g}^{-1} \text{min}^{-1}$)	R^2
Pb	68	9.134	0.430	95.29	2.53×10^{-2}	0.873	9.17	0.394	2.42×10^{-1}	1
	74	6.442	2.355	63.44	6.78×10^{-2}	0.943	6.57	1.98	7.33×10^{-2}	0.999

Pseudo-second-order kinetic model

The pseudo second order equation is expressed as:

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

where k_2 is the kinetic rate constant ($\text{mg g}^{-1} \text{min}^{-1}$) [17].

The values of $q_{e,cal}$ and k_2 were calculated from the linear plot of t/q_t vs t with slope $1/q_e$ and intercept $1/k_2 q_e^2$ [Fig.7(b)]. The values of k_2 ,

$q_{e,cal}$ and the correlation coefficient R^2 obtained from the plots are presented in Table 2. The results show that the R^2 values were nearly unity indicating the applicability of Pseudo-second-order kinetic model to describe the adsorption process of Pb(II) on MCM-41. The $q_{e,cal}$ values also agreed well with the experimental data, $q_{e,exp}$.

CONCLUSION

The synthesis of mesoporous MCM-41 was done successfully and its effect on the removal of Pb(II) from aqueous solution in batch experiments under a variety of operating conditions was investigated. The adsorption was found to be drastically dependent on contact time, adsorbent dosage, initial metal ion concentration. The results of this study indicated that the uptake of Pb(II) increased with an increase in contact time and adsorbent dosage for the same initial concentration. As usual, the removal percentage of metal ion decreased with increasing initial metal concentration in aqueous solutions keeping other parameter constant. Kinetic data were adequately fitted by the pseudo-second-order kinetic model. It can be concluded that mesoporous MCM-41 can be used as an effective adsorbents for the removal of Pb(II) from aqueous solution.

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