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deparment of chimical engineering

Research

Keywords: Cadmium, Lead, Binary system, MCM-48, Adsorption

Posted Date: January 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-148452/v1>

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Comparative adsorption of Cd(II) and Pb(II) by MCM-48 and amine-grafted MCM-48 in single and binary component systems

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ABSTRACT

MCM-48 were prepared using hexadecyl trimethyl ammonium bromide and TEOS and modified with N¹-(3-Trimethoxy silylpropyl) diethylenetriamine by post-synthesis method, in order to develop efficient adsorbent for heavy metal adsorption. These materials were determined by X-ray diffraction, N₂ adsorption–desorption measurement and Scanning Electron Microscopy. The results show that the modification of MCM-48 resulted in decrease in the Brunauer-Emmett-Teller surface area and total pore volume. Batch adsorption technique in single and multi-component system was used in this study. The influence of experimental parameters was investigated and the results indicated that amine attached MCM-48 indicated

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higher adsorption efficiency for metal ions than MCM-48. Langmuir and Freundlich models modeled the equilibrium data in single system; whereas two component data fitted to the extended Langmuir model. The maximum adsorption capacity (q_m , single system) of NH₂-NH-NH-MCM-48 for cadmium and lead was 82.7 mg g⁻¹ and 119.24 mg g⁻¹, respectively. In both adsorption systems, the affinity of NH₂-NH-NH-MCM-48 for cadmium was greater than that for lead.

Keyword: Cadmium; Lead; Binary system; MCM-48; Adsorption.

1. Introduction

Heavy metal contamination has turned into a one of the most significant environmental issues today, because they are poisonous and carcinogenic, even in low concentration, can accumulate throughout the food chain [1-3]. Lead and cadmium are dangerous heavy metals. Several techniques for heavy metal elimination from wastewater is available such as filtration [4], reverse osmosis [5], coagulation – flocculation, ion exchange [6], precipitation [7] and adsorption [8, 9]. Adsorption has developed one of the few promising method for treatment of industrial wastewater, especially using efficient adsorbent.

Mesoporous silica materials have capability to be use in the field of environment, due to the high surface area, specific structure, narrow pore size distribution, homogeneous pore size and their biocompatibility [10-12]. Surface functionalization of ordered mesoporous silica with different functional groups such as amines is important to acquire large adsorption capacity. Recently, the functionalization of MCM-48 have been studied. For example, Faghihian and Naghavi [13] synthesized amine-functionalized MCM-48 and used as adsorbent for treatment of Cu(II), Co(II), Cd(II), and Pb(II) from artificial wastewater.

In this study, MCM-48 was synthesized and functionalized and used for comparative adsorption of Cd (II) and Pb (II) ions from aqueous solution in single and multi-component

system study. The influence of various adsorption conditions on the removal performance of Cd (II) and Pb (II) actions were examined.

2. Materials and methods

2.1 Materials

In this study, hexadecyl trimethyl ammonium bromide, n-hexane, toluene and hydrochloric acid (37%) from Merck Co., sodium hydroxide, tetraethoxy silane 98%, N¹-(3-Trimethoxy silylpropyl) diethylene triamine from Sigma-Aldrich Co, , CdCl₂ and Pb(NO₃)₂ from Sigma Aldrich Co were purchased.

2.2 Synthesis of MCM-48

MCM-48 was prepared based on the method of wang et al [14]. The source of silica was tetraethoxy silane and hexadecyl trimethyl ammonium bromide was used as surfactant. Typically, 10 mL of TEOS was added to 50 mL of deionized water. The above mixture was agitated and heated at 35 °C for 40 min. Then, 0.6 g of NaOH was added to the mixture under string. After 1h agitated at 35 °C, 10.61 g of CTAB added to the gel under agitation for 1 h at 110° C. Then the resulting homogenous mixture transferred into a bottle and inserted into an oven at 120 °C for 24 h to the crystallization was performed. After that, the obtained material was filtered and washed with deionized water several times. The synthesized MCM-48 was dried at the room temperature and then calcined for 6 h at 550° C with heating rate of 2 °C/min.

2.3 Synthesis of amine-functionalized MCM-48

The amine-functionalized MCM-48 (NH₂-NH-NH-MCM-48) was synthesized based on the procedure of Yokoi et al [15]. Briefly, 0.5 g of calcined MCM-48 was suspended in 100 mL of the dry toluene and stirred for 30 min, and then 1 mL of N¹-(3-Trimethoxy silylpropyl) diethylene triamine (modifying agent) was added to the mixture and refluxed for 8 h at 60 °C. The obtained material was washed with n-hexane and toluene several times, dried and stored in a desiccator.

2.4 Characterization

X-ray diffraction (XRD) patterns of MCM-48 and NH₂-NH-NH-MCM-48 were attained using XRD diffractometer (X'pert, Phillips, and Holland). Nitrogen adsorption-desorption isotherms of the adsorbents were measured at 77 K using a Micromeritics Instrument Model ASAP 2010. The surface shape of MCM-48 were observed by scanning electron microscopy (SEM, Phillips XL30, and Holland).

2.5 Adsorption experiments

Batch process was employed onto the MCM-48 and NH₂-NH-NH-MCM-48 at room temperature in single and binary systems. All experiments were done three times. A stock solution of cadmium and lead (1000 mg L⁻¹) ions was prepared by dissolving an proper amount of Pb(NO₃) and Cd(Cl)₂ in deionized water. For each experiment, 100 mL of aqueous solution of these metals in different concentration were place in 250 mL Erlenmeyer flasks. During adsorption process, the samples gotten at different time intervals; the supernatant was filtered with 0.45 µm filter paper (Whatman) to ensure that mesoporous particles were removed. The concentration of cadmium and lead ions in the supernatant remaining was measured by atomic absorption spectroscopy. The pH of metal ion aqueous solution was adjusted to 6 by adding NaOH and HCl (0.1 M). The removal efficiency (%) and the adsorption capacity (mg g⁻¹) was considered by the following calculations:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$qe = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where, R (%) is the metal removal percentage, C_0 (mg L⁻¹) is the initial metal concentration, C_e (mg L⁻¹) is the equilibrium metal concentration, q_e (mg g⁻¹) is the equilibrium adsorption capacity of adsorbent, V (L) is the volume of solution, and m (g) is the quantity of the adsorbent.

2.6. Equilibrium and adsorption studies

2.5.1 Adsorption isotherms

The Langmuir and Freundlich models are the most usual types of models which widely used to describe the adsorption of metal ions by adsorbents. Langmuir equation model can be expressed by [14] [16]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the equilibrium metal concentration, q_m (mg g^{-1}) is the maximum adsorption capacity, and K_L (mg L^{-1}) is constant associated to the adsorption bonding energy. Freundlich model is given by:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where K_F (mg L^{-1}) and $1/n$ are the Freundlich coefficients indicative of the relative adsorption capacity, and the intensity of adsorption.

The Langmuir competitive model (LCM) is an extended configuration of the Langmuir model to evaluate the experimental binary adsorption data of lead and cadmium. The CML isotherm equation is given as follows [17-21]:

$$Q = \frac{K_{L1} q_m C_{e1}}{1 + K_{L1} C_{e1} + C_{e2} K_{L2}}$$

(5)

Where K_{L1} and K_{L2} (L mg^{-1}) are the constants depicted by fitting the Langmuir model to the single component adsorption data.

2.5.2 Adsorption kinetics

The pseudo-first-order kinetic and the pseudo-second-order kinetic models are given by [22-24]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

(7)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where q_e and q_t (mg g^{-1}) are the equilibrium adsorption capacity and adsorption capacity at t time, K_1 and K_2 ($1/\text{min}$) are the rate constants of pseudo-first-order and pseudo-second-order, respectively. The q_e , K_1 and K_2 were calculated from the slope and the intercept of plots of equation 7 and 8.

2.5.3 Desorption and Regeneration

Desorption and regeneration experiments were carried out using MCM-48 and $\text{NH}_2\text{-NH-NH-MCM-48}$ adsorbents at the batch process, separately. After adsorption experiment, the adsorbent was separated from the solution by centrifugation and subsequently washed with distilled water, dried in an oven at 60°C and weighted. Then, it suspended in 100 mL of HNO_3 solution desorption agent. The mixture was agitated for 120 min and centrifuged. The concentration of metal ions was measured. For reuse of the spent adsorbent after adsorption, the residue sludge from desorption study was washed, dried and weighted. Then, it used for adsorption experiments. The Adsorption study of cadmium and lead onto these adsorbents have follow conditions: initial metal concentration of 10 mg L^{-1} , adsorbent quantity of 0.5 g L^{-1} , pH of 5, string speed of 200 rpm, room temperature and reaction for 20 min. The detailed of adsorption procedures were the described in Sections 2.5. The adsorption- desorption cycles of the adsorbents were repeated 5 times under same condition. The adsorption recovery was calculated by [25]:

$$\text{Desorption recovery} = \frac{\text{Quantity of metal desorbed to elution medium}}{\text{Quantity of metal adsorbed on adsorbent}} \times 100 \quad (9)$$

3. Results and discussions

3.1 Characterization of adsorbents

Fig. 1 shows the XRD spectra of MCM-48. The XRD pattern of MCM-48 displays strong (211) peak and proportional (220) peak at the low angle region of $2\theta = 3.2^\circ\text{-}3.55^\circ$, indicating the

cubic phase of MCM-48 materials. Several other diffraction peaks with lower intensities are shown in the high angle region of $2\theta = 4^\circ$ - 6° , which can be indexed (321), (400), (420), (322), (422), (431), (611) and (543) diffraction peaks. These findings indicate the presence of highly ordered cubic pores in the structure of MCM-48.

The adsorption-desorption isotherms of nitrogen at 77 K on MCM-48 and amine grafted MCM-48 were investigated (figure not shown). The MCM-48 isotherm presents a type IV profile based on IUPAC classification with H1 hysteresis loops, which indicated mesoporous material, while after the modification with amine group (NH₂-NH-NH-MCM-48 adsorbent) illustrated the type I isotherm, which is typical of microporous solids. The Brunauer-Emmett-Teller (BET) surface area, pore volume and the average pore size of these adsorbents were determined. The surface area of MCM-48 and total pore volume decreased from 1062 m²/g to 736 m²/g and from 1.743 cm³/g to 0.343 cm³/g respectively, after grafting with functional ligand. This is most likely because of the setting down of the amine functionalized groups on the pores of the adsorbents [26]. The SEM image of MCM-48 is illustrated in Fig. 1. As presented in Fig. 1, MCM-48 typically has a sphere-like shape.

Fig. 1 displays the FTIR spectra of MCM-48 and NH₂-NH-NH-MCM-48 in the 400-4000 cm⁻¹ region. The absorption bands at 463 cm⁻¹ and 802 cm⁻¹ related to the asymmetric and symmetric vibration of Si-O-Si band [27, 28]. The band appeared at 1080 cm⁻¹ was also Si-O-Si band [27, 28]. A broad band in 3449 cm⁻¹ and 3417 cm⁻¹ are ascribed to the stretching band of Si-O-H [29]. The weak peak located at 1636 cm⁻¹ attributed to the bending vibration of adsorbed water molecules [30]. Compared to the MCM-48, the NH₂-NH-NH-MCM-48 shows the peaks at 2916 cm⁻¹ and 2847 cm⁻¹ related to the CH₂ stretching modes [30, 31]. Also, the absorption band at 1543 cm⁻¹ was corresponded to the NH₂ bending [31]. It confirmed that the amine groups were incorporated into the silica structure through functionalization successfully.

3.2 Adsorption study

3.2.1 Effect of adsorbent dose

The effect of different quantity of MCM-48 and NH₂-NH-NH-MCM-48 (0.125, 0.5, 1.25, 2.5, 5, 7.5 and 10 g L⁻¹) on the adsorption of Cd (II) and Pb(II) metal ions was studied. The experiments were carried out at pH 6, contact time of 120 min, initial metal concentration of 50 mg L⁻¹ and room temperature. Their results were shown in Fig. 2. As seen in this figure, the percentage removal of metal ions increases significantly with increase in both adsorbent dosage from 0.125 g L⁻¹ to 5 g L⁻¹ and tended to reach a saturation level in the range of 5 g L⁻¹ to 10 g L⁻¹. Furthermore, for both adsorbents and both metal ions, the increment in adsorption capacity, q_e , was depicted with increase in adsorbent dosage (Fig. 2). This can be explained by increment in BET surface area which lead to the accessibility of extra binding sites for adsorption [32]. It is known that the maximum metal ions removal was obtained at about 10 g L⁻¹ of MCM-48 and NH₂-NH-NH-MCM-48. As shown in Fig. 2 (a and b) 10 g L⁻¹ of MCM-48 and NH₂-NH-NH-MCM-48 remove 37% and 95% of Cd(II) and 34% and 88.5% of Pb(II), respectively. In the experiments, an adsorbent dose of 0.5 g L⁻¹ of MCM-48 and NH₂-NH-NH-MCM-48 was used.

3.2.2 Effect of the pH

To investigate the influence of the pH on the adsorption of cadmium and lead ions by MCM-48 and NH₂-NH-NH-MCM-48, adsorption experiments were conducted in pH range of 2 to 6 keeping all other parameters constane (the adsorbent dose of 0.5 g L⁻¹, initial metal oncentration of 10 mg L⁻¹ and contact time 2h). This range was chosen because the lead precipitate at pH > 6 according to solubility rules, as examined in previous studies [25, 33, 34]. The results were presented in Fig. 3. From this graph, it observed that as the pH of solution increased from two to six, the adsorption capacity of Cd (II) metal ion on both adsorbents increased up to pH 5 and then decreased at pH 6. This trend was also observed for Pb (II) metal ion, while the q_m was

attained at pH 4 instead of pH 5. Besides, the maximum removal of cadmium and lead ions onto MCM-48 and NH₂-NH-NH-MCM-48 was obtained at pH of 5 and 4, respectively.

To explain this observation, at low pH, the higher concentration and high mobility of the hydrogen ions was observed which directly compete with the metal ions for active binding sites in the adsorbents; the overall surface charge on the adsorbent gets positive and repellents the lead and cadmium cations. At the pH higher than five, the amount of dominant metal ions (M) species in aqueous solution are M(OH)₂. Furthermore, the low solubility metal hydroxides results in the precipitation of metals, thereby the cations are not accessible to adsorb by adsorbents, reducing adsorption capacity [35, 36].

3.2.3 Adsorption Isotherm

The experimental adsorption data on the effect of an initial concentration of Cd (II) and Pb (II) metal ions range 10 mg L⁻¹ to 50 mg L⁻¹ onto MCM-48 and NH₂-NH-NH-MCM-48 were fitted to Langmuir and Freundlich isotherm models. The nonlinearized adsorption isotherms of these models are presented in Fig. 4 a and b while the various parameters are reported in Table 1. The plot of C_e/q_e versus C_e show that the experimental data fitted reasonably to the both isotherms. The Langmuir model yields better fit than the Freundlich model, in terms of the high correlation coefficient ($R^2 > 0.98$). The q_m estimated by Langmuir model. For both metal ions, NH₂-NH-NH-MCM-48 has higher q_m than MCM-48 which was 82.7 mg g⁻¹ and 119.24 mg g⁻¹ for Cd (II) and Pb(II), respectively. Higher q_m and K_L values for Pb (II), as compared to Cd (II) present the stronger binding affinity of MCM-48 and NH₂-NH-NH-MCM-48 to Pb (II) to that to Cd (II). This attributed to the higher atomic weight, electronegativity, electrode potential and ionic size of lead compared to cadmium [30]. The freundlich constant (K_f and n) demonstrate whether the nature of adsorption is either favourable or unfavourable [37]. For both adsorbents, the values of n were between 1 and 10, indicate favorable adsorption.

Adsorption kinetics

Adsorption kinetics of Cd (II) and Pb (II) metal ions uptake by NH₂-NH-NH-MCM-48 adsorbents were investigated based on experimental data and the values of the constants obtained are listed in Table 2. From Table 2, it can be seen that the correlation coefficients (R^2) values of pseudo-second-order kinetic model for all concentrations (except 60 mg L⁻¹ lead) are almost higher than R^2 values of other model. Besides, the q_e obtained from this model were more consistent with the experimental values of adsorption capacities. Therefore, pseudo-second-order kinetic model seemed to be appropriate model for predicating the kinetics of Cd (II) and Pb (II) metal ions adsorption by onto NH₂-NH-NH-MCM-48. In addition, it suggests that chemisorption occurred during adsorption process of heavy metal ions by functionalized mesoporous silica.

3.2.4 Binary adsorption of lead and cadmium metals

Competitive adsorption of cadmium and lead metal ions from their binary system was examined to simulate the real environmental conditions where the application is planned are complex. The LCM predicted the complete adsorption behavior of metal ions onto NH₂-NH-NH-MCM-48 with $R^2 > 0.99$ for Pb (II) and $R^2 > 0.99$ for Cd (II) metal ions. As shown in Table 1, q_m values obtained from the Langmuir model in the binary adsorption system was 50 mg g⁻¹ 73 mg g⁻¹ for cadmium and lead, respectively, which were lower than those calculated in single adsorption system. It could be attributed to interfere and completion one metal ion in adsorption of the other in binary system.

The preference of the adsorption of a metal ion compared to another by adsorbent in binary system is important. The influence of bi-solute competition on adsorption of lead and cadmium was also evaluated by using the ratio of the adsorption capacity of one metal, i , at equilibrium, in the presence of other metal, j , q_{mL}^* , to the adsorption capacity of corresponding metal in single metal system, q_{mL} . When the ratio q_{mL}^* to q_{mL} is higher than one, synergism; the adsorption is promoted by the presence of the other metal ion. For the ratio q_{mL}^* to q_{mL} equal to

one, non-interaction; there is no obvious interaction between j and I. For the ratio q_{mL}^* to q_{mL} lower than 1, antagonism; the adsorption of species i is suppressed by the presence of the species j [38]. The values of maximum adsorption capacity of NH₂-NH-NH-MCM-48 for Pb (II) and Cd (II) decreased in binary system compared to single system, confirming that the adsorption of these metal ions is suppressed at the presence of the another metal and competitive adsorption in binary metal system.

Pb exhibited higher maximum adsorption capacity (73 mg g⁻¹) than Cd (50 mg g⁻¹) in binary component systems due to more competition ability to bind with free amine groups on adsorbent. This could be related to the difference in metal class behavior based on their covalent index [39, 40]. The covalent index is calculated as follows [41]:

$$\text{Covalent index} = X_m^2(r + 0.85) \quad (10)$$

Where, X_m and r represent the electronegativity and radius of metal ion, respectively. The obtained covalent index of Pb (II) and Cd (II) were 11.8 and 5.6, respectively. According to covalent index, Pb (II) is considered as a class b ions while Cd is classified as borderline ion [39, 40]. On the basis of this argument, the greater covalent index caused in the greater affinity between heavy metal ions (Pb²⁺ and Cd²⁺) and adsorbent ligand (-NH₂ groups). As results, Pb (II) has a higher q_m with NH₂-NH-NH-MCM-48 than Cd (II).

3.2.5 Comparison with other adsorbents

Table 3, shows the values of Langmuir adsorption capacity (q_m) for the adsorption of Cd (II) and Pb (II) on different mesoporous silica adsorbents reported in the literature. As shown in Table 3, chen et al [42] prepared Ti-MCM-48 for adsorption of Cd (II) cation and the obtained q_m was 83.5 mg g⁻¹ which those were the near the q_m acquired in this study (82.7 mg g⁻¹). The adsorption capacity of mesopressure silica is influenced by two factors: (1) type of mesoporous silicate, (2) density of the amine groups bonded to silica [15, 43, 44]. Faghihian and Naghavi functionalized MCM-48 with amino-ethylamino]-propyltrimethoxysilane (NN-MCM-48). The

obtained values of q_m were found to be 93.4 and 147 mg g⁻¹ for Cd and Pb, respectively. The q_m for Cd and Pb with NNN-MCM-48 in this study were 82.7 and 119.2 mg g⁻¹, respectively. This reduction in adsorption capacity is probably due to the low density of amine groups in the mesoporous structure. This is in agreement with the Yokoi et al [15] findings. They modified MCM-41 with mono-, di- and tri-amino-organoalkoxysilanes and used for heavy metal adsorption. Their results indicated that the q_m was improved with increment in the density of amino functional groups. Moreover, the adsorption capacities of heavy metals decreased when NNN silane was grafted to the meoporouse surface. Furthermore, the q_m reported by Benhamou *et al* [45] for Cd (II) and Pb (II) cations using N-N dimethyldodecylamine and dodecylamine grafted MCM-48 and those obtained by Aniba *et al* [46] with magnetic mesoporous silica MCM-48 modified with melamine-based dendrimer amine, were higher than those in this research. The reason for the high q_m in these study can be associated to other factors such as the availability of amine groups and branched-chain of amine group in mesoporous structure that have positive effect on adsorption [47, 48]. Beside, other members of mesoporous silica family such as amine grafted MCM-41 and SBA-15 showed higher q_m for Cd and Pb due to having different pore size and surface area. Da'na [44] found that silica structural order, pore size, and surface area are significant parameters of mesoporous material to determine their affinity to adsorption heavy metal ions.

3.2.6 Desorption study

Desorption of lead and cadmium metal ions from MCM-48 and NH₂-NH-NH-MCM-48 using HNO₃ as a desorbing agent into desorption medium was investigated. The results related to the removal of the amount of ions desorbed and adsorption capacity after five successive adsorption – desorption cycles are shown in Table 4. As can be seen from Table 4, the dominant part of metal was removed in the first desorption cycle and HNO₃ was efficient in desorbing the metal ions, especially NH₂-NH-NH-MCM-48. For example, the desorption efficiency of Pb(II)

metal ion by this adsorbent was about 84.5 % in the first cycle, and in 2, 3, 4 and 5 cycles was 79.4, 75, 68.6 and 61.9%, respectively. For MCM-48, at first cycle, the obtained maximum removal was 35.3 and 32 % for cadmium and lead, respectively and it decreased at next cycles. Furthermore, the results of re-adsorption of Cd (II) and Pb(II) ions using both the spent adsorbents demonstrate that the adsorbents could be reused up to 5 times but their adsorption capacity decreased, but this reduction was not significant for NH₂NHNH-MCM-48 adsorbent.

4. Conclusion

The efficiency of MCM-48 and amine-functionalized MCM-48 (NH₂-NH-NH-MCM-48) for the competitive adsorption of cadmium and lead was examined. The characteristics of these adsorbents were determined by XRD, SEM and N₂ adsorption-desorption. The batch adsorption experiments were conducted in single and binary systems and the effects of adsorbent dosage, pH, contact time and initial metal concentrations were studied. With both adsorbents, the optimal pH for removal of cadmium and lead was 5 and 4, respectively. The Langmuir and Freundlich isotherm models were fitted with the adsorption experimental data, and the Langmuir equation indicated better fit than the Freundlich model, in terms of the higher correlation coefficients. According to the Langmuir model, for both metal ions, NH₂-NH-NH-MCM-48 has higher maximum adsorption capacity than MCM-48, which was 82.7 mg g⁻¹ and 119.24 mg g⁻¹ for cadmium and lead, respectively. The binary- metal mixture adsorption results confirm that the adsorption of these metal ions is suppressed at the presence of the metal. The two-component equilibrium data were fitted to the modified extended Langmuir.

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Table 1, Adsorption parameters of the Langmuir and Freundlich isotherm models for the Cd(II) and Pb(II) adsorption onto MCM-48 and NH₂-NH-NH-MCM-48.

Adsorbent	Metal ion	Langmuir			Freundlich			Langmuir competitive model (LCM)		
		R^2	$b, \text{ l mg}^{-1}$	$q_m, \text{ mg g}^{-1}$	R^2	n	K_f	R^2	$b_L, \text{ l mg}^{-1}$	$q_{mL}, \text{ mg g}^{-1}$
MCM-48	Cd(II)	0.982	0.060	29.13	0.942	2.09	3.50			
	Pb(II)	0.989	0.026	50.39	0.973	1.52	2.25			
NH ₂ -NH-NH-MCM-48	Cd(II)	0.988	0.071	82.70	0.954	1.86	9.28	0.992	0.055	50
	Pb(II)	0.989	0.133	119.24	0.952	1.91	19.04	0.935	0.025	73

Table 2, Kinetic adsorption parameters obtained using pseudo-first-order and pseudo-second-order models onto NH₂-NH-NH-MCM-48

Metal ions	Metal cons., mg L ⁻¹	q _{exp} , mg g ⁻¹	Pseudo-first-order			Pseudo-second-order		
			K ₁ , min ⁻¹	q _{e1} , mg g ⁻¹	R ²	K ₂	q _{e2} , mg g ⁻¹	R ²
Cd(II)	5	4.92	0.009	3.08	0.903	0.016	5.14	0.990
	10	9.52	0.007	7.48	0.918	0.003	10.4	0.913
	20	18.2	0.007	14.09	0.939	0.002	19.6	0.935
	30	24.2	0.008	19.18	0.967	0.001	26.8	0.968
	40	27.9	0.010	21.94	0.962	0.001	30.8	0.974
	50	29.4	0.008	19.16	0.896	0.001	30.6	0.978
	60	30.1	0.008	28.48	0.937	0.000	37.1	0.859
Pb(II)	5	7.22	0.010	4.53	0.906	0.011	7.58	0.982
	10	14.2	0.008	9.36	0.905	0.004	14.9	0.975
	20	27.9	0.010	20.53	0.943	0.002	30.2	0.973
	30	39.7	0.009	27.89	0.948	0.001	42.3	0.981
	40	49.2	0.008	38.07	0.931	0.000	53.7	0.947
	50	58.4	0.010	45.40	0.973	0.000	64.5	0.983
	60	59.9	0.010	47.44	0.972	0.000	66.2	0.975

Table 3, Comparison of the Langmuir maximum adsorption capacity of Pb (II) and Cd (II) metal ions onto some mesoporous silica adsorbents.

Adsorbents	$q_{\max}$ (mg g ⁻¹)		Ref
	Cd (II)	Pb (II)	
MCM-48	29.13	50.39	This study
NH ₂ -NH-NH-MCM-48	82.7	119.24	
NH ₂ -NH-NH-MCM-48 ^a	50	73	
NN-MCM-48	93.4	147	
Ti-MCM-48	83.57	-	Faghihian and Naghavi, 2014
N-N dimethyldodecylamine grafted MCM-48	175.35 (1.56) ^b	238.28 (1.15) ^b	
Dodecylamine grafted MCM-48	148.38 (1.32) ^b	194.76 (0.94) ^b	Benhamou <i>et al</i> , 2009)
Melamine grafted magetic-MCM-48	114.08	127.24	
NH ₂ -MCM-41	18.25	57.74	Aniba <i>et al</i> , 2015
NH ₂ -MCM-41	90.92	-	Heidari et al, 2009
MDA-SBA-15	98	130.1	Ghorbani et al, 2013
			Shahbazi et al, 2011)

^a q_m in binary system

^b mmol/g

Table 4, Desorption of Cd(II) and Pb (II) metal ions by MCM-48 and NH₂-NH-NH-MCM-48

Metal ion	Adsorbent	Parameter	Number of cycles				
			#1	#2	#3	#4	#5
Cd (II)	MCM-48	R, (%)	35.30	29.19	25.84	20.71	13.61
		q_e , (mg g ⁻¹)	7.16	5.92	5.24	4.2	2.76
	NH ₂ NHNH-MCM-48	R, (%)	66.69	62.15	56.71	49.20	37.54
		q_e , (mg g ⁻¹)	13.5	12.58	11.48	9.96	7.6
Pb (II)	MCM-48	R, (%)	32.07	28.88	22.71	19.12	16.13
		q_e , (mg g ⁻¹)	6.44	5.80	4.56	3.84	3.24
	NH ₂ NHNH-MCM-48	R, (%)	84.47	79.43	75.00	68.54	61.89
		q_e , (mg g ⁻¹)	16.76	15.76	14.88	13.60	12.28

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Fig. 1 SEM image, XRD pattern, and FTIR spectra of MCM-48 (a) and NH₂-NH-NH-MCM-48.

Fig. 2 Effect of adsorbent dosage of MCM-48 and NH₂-NH-NH-MCM-48 on the adsorption of (a) Cd (II) and (b) Pb (II) metal ions.

Fig. 3 Effect of solution pH on the adsorption of (a) Cd (II) and (b) Pb (II) metal ions with MCM-48 and NH₂-NH-NH-MCM-48.

Fig. 4, Langmuir, Freundlich and Langmuir competitive adsorption isotherms of (a and c) Cd (II) and (b and d) Pb(II) onto MCM-48 and NH₂-NH-NH-MCM-48.

Figures

Figure 1

SEM image, XRD pattern, and FTIR spectra of MCM-48 (a) and NH₂-NH-NH-MCM-48.

Figure 2

Effect of adsorbent dosage of MCM-48 and NH₂-NH-NH-MCM-48 on the adsorption of (a) Cd (II) and (b) Pb (II) metal ions.

Figure 3

Effect of solution pH on the adsorption of (a) Cd (II) and (b) Pb (II) metal ions with MCM-48 and NH₂-NH-NH-MCM-48.

(a)

(b)

Figure 4

Langmuir, Freundlich and Langmuir competitive adsorption isotherms of (a and c) Cd (II) and (b and d) Pb(II) onto MCM-48 and NH₂-NH-NH-MCM-48.