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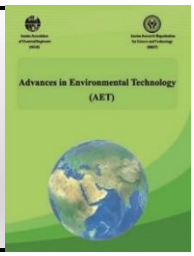

Kinetic study of Pb (II) and Ni (II) adsorption onto MCM-41 amine-functionalized nano particle

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ABSTRACT

In the current investigation a novel nano hybrid adsorbent MCM-41/N-(3-trimethoxysilyl)-propyl) diethylenetriamine (MCM-41/TMSPDETA) was prepared and was characterized using DLS (Dynamic Light Scattering), Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analytical techniques and Transmission electron microscopy (TEM). The synthesized MCM-41/TMSPDETA adsorbent possessed high surface area (867 m^2g^{-1}), narrow pore size distribution (3.6 nm) and pore volume (0.782 cm^3g^{-1}). The nano hybrid adsorbent was applied in batch experiments under different controlling factors by varying pH, contact time and solution temperature of Lead (Pb(II)) and Nickel (Ni(II)) ions. Optimum conditions obtained were 20°C, pH=6 and contact time of 120 min. The maximum capacity of the nano-sorbent was obtained to be 58.823 and 20.921 mg g^{-1} for Pb (II) and Ni (II) ions for an initial concentration range 10-70 mgL^{-1}. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyze the kinetic data. Results showed that the pseudo-second order model can well describe the adsorption kinetic data.

1. Introduction

In recent years, Heavy metals pollution has attracted a great deal of attention, especially Lead and Nickel as serious environmental threats. Lead and Nickel pollution results from battery manufacturing, textile dying, petroleum refining, ceramic and glass industries and mining operations [1]. Lead and Nickel may cause retardation, mental disturbance and semi-permanent brain damage [2]. Therefore, the development of clean-up technologies for removing heavy metals from wastewaters is very important.

The removal of toxic metals from wastewaters can be carried out by a number of separation technologies, such as chemical precipitation [3], membrane processes [4], solvent extraction, ion exchange [5], floatation, coagulation and sorption process [6]. Among these methods, sorption is currently considered to be very suitable for wastewater treatment because of its high efficiency, simple operation and cost effectiveness [7]. A number of effective adsorbents have been prepared and reported in recent years [8]. Mesoporous silica materials have received considerable attention due to their unique large surface area, well-defined pore size and pore shape. One of these materials, MCM-41, consists of hexagonal arrays of large and uniform pore size, large surface area, thermal stability and mild acidic property [9]. Mesoporous silica MCM-41 has been functionalized and employed to eliminate traces of toxic heavy metal from wastewater [10]. Amino functional mesoporous silica MCM-41 materials have been prepared to develop efficient adsorbents of heavy metals in wastewater.

The literature studies on the removal efficiency of functionalized mesoporous silica for Pb (II) and Ni (II) are limited. Adsorption of Pb (II) ion with nano MCM-41/TMSPDETA has not been reported.

The structure of the prepared nano adsorbents surface was characterized using DLS (Dynamic Light Scattering), Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and Transmission electron microscopy (TEM) analytical techniques. The goal of the present paper was the sorption of Pb (II) and Ni (II) on MCM-41/TMSPDETA nano adsorbent. The influence of pH, contact time and solution temperature on the sorption

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process were investigated. Also, kinetic models (Pseudo-first order, pseudo-second order and intraparticle diffusion) were established.

2. Material and Methods

2.1. Materials

Hexadecyltrimethylammoniumbromide (CTAB); Tetraethoxysilane (TEOS), *N*-(3-trimethoxysilyl)-propyl) diethylenetriamine (TMSPDETA) were purchased from Aldrich Co. CH_3OH, HCl and $NaHNO_3$ were provided by Merck Co. Sources of metal for sorption experiments were $Pb(NO_3)_2$ and $Ni(NO_3)_2$ of synthesis grade that were supplied from Merck Co. Heavy metal solution (Pb^{2+}) was prepared by dissolving weighed amount of uranyl nitrate (Aldrich) in deionized water. Deionized water was utilized throughout this experiment. Infrared spectra were recorded on a Fourier transform infrared (FT-IR) spectrometer (Shimadzo, FTIR1650 spectrophotometer, Japan) in the range of 400–4000cm^{-1} using spectroscopic quality KBr powder (sample/KBr = 1/100). The residual concentrations of Pb (II) and Ni (II) ions were determined by an inductivity coupled plasma atomic emission spectrophotometer (Shimadzu AA-670).

2.2. Amino-functionalized MCM-41 via direct co-condensation method

The synthesis of functionalized MCM-41 with N silane via the co-condensation method was conducted as follows. CTAB and NaOH were dissolved in deionized water while heating. Afterwards the Si sources (TEOS) were added to the above mixture. Then *N*-(3-trimethoxysilyl)- propyl) diethylenetriamine (TMSPDETA) was added to the mixture and the solution was stirred 300 rpm for 4 h. The surfactant in the as-synthesized sample was removed by a solvent extraction method; 1.0 g of the as-synthesized sample was stirred in a HCl/MtOH solution (100 ml of methanol containing 5 ml HCl aq. Concentration ca. 35 wt%) at 298 K for 24 h.

2.3. Adsorption experiments

Adsorption experiments were conducted in a batch way. Each experiment was carried out by placing specific amount of nano-adsorbent of MCM-41/ TMSPDETA in aqueous solutions under various operating conditions. The initial Pb (II) and Ni (II) ions concentration of 30 mg/L, contact time of 2h, and adsorbent dose values were varied between 1 and 5 g/l. The effect of contact time was investigated by varying the time from 5 to 120 min, at a temperature of 25 °C. The sorption capacity for heavy metal ions was determined as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 and C_e (mg/L) are the initial and final metal ion concentrations, respectively; V is the volume of solution (L) and m is the weight of adsorbent (g).

3. Results and discussion

3.1. Adsorbent characterization

From DLS (Dynamic Light Scattering), the hydrodynamic particle size of the silica functionalization with amine group, MCM-41/TMSPDETA was estimated to be approximately 627.2nm (Figure 1).

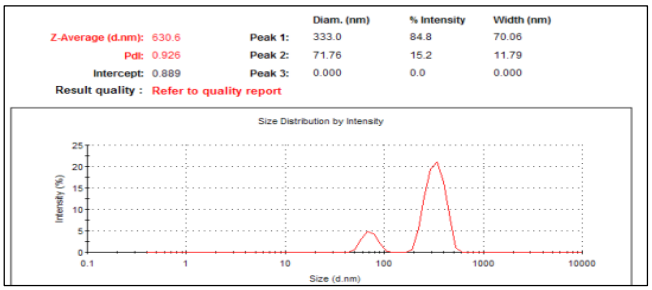

Figure 1. DLS (Dynamic Light Scattering) of the hydrodynamic size.

Infrared technique was used for identification of nano adsorbent. After functionalization with amine group, MCM-41/TMSPDETA showed visible broad absorption bands at 1560cm^{-1} and at 1650cm^{-1} corresponding to the bending vibration of N–H group, while N–H stretching (3200–3500 cm^{-1}) and C–N stretching (1030–1230cm^{-1}) overlap with the broad absorption bands of the silanol group and the Si–O–Si vibrations (Figure 2).

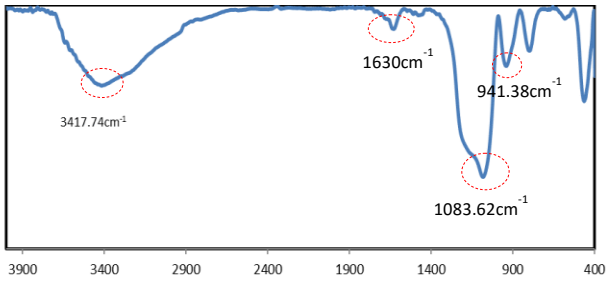

Figure 2. FT-IR spectra of MCM-41/ TMSPDETA.

The XRD pattern of MCM-41/TMSPDETA is shown in Figure 3. As can be seen, the broad peaks indicate the nano-crystalline nature of the particles.

In Table 1. the adsorbed nitrogen volume indicated the mesoporous silica materials functionalized with TMSPDETA have more sorption nitrogen volume, which is attributable to the presence of lower amino groups. The specific surface area of MCM-41 decreased from 1063 to 867 m^2/g when it was functionalized with amine group41/TMSPDETA

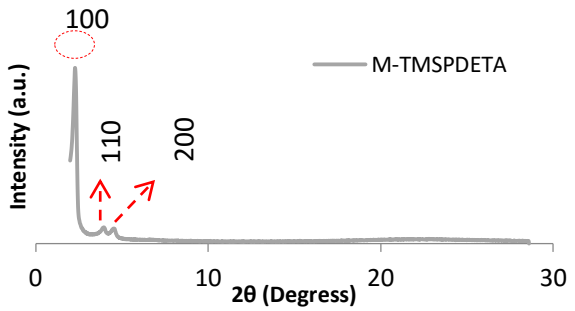

Figure 3. X-ray diffraction patterns of MCM-41 and MCM-41/TMSPDETA.

Table 1. Physicochemical properties of extracted-MCM-41 and MCM-41/TMSPDETA.

Samples	S_{BET} (m^2/g)	V_p (cm^3/g)	d_{BJH} (nm)	$d_{avg.}$ (nm)
MCM-41	1063	1.082	3.88	4.03
MCM-41/TMSPDETA	867	0.782	3.61	3.81

The determined-field TEM image at high magnification of the MCM-41/TMSPDETA showed a lamellar mesostructure with a well-defined hexagonal arrangement of uniform pores. The pore size was estimated to be ~3.4 nm (Figure 4).

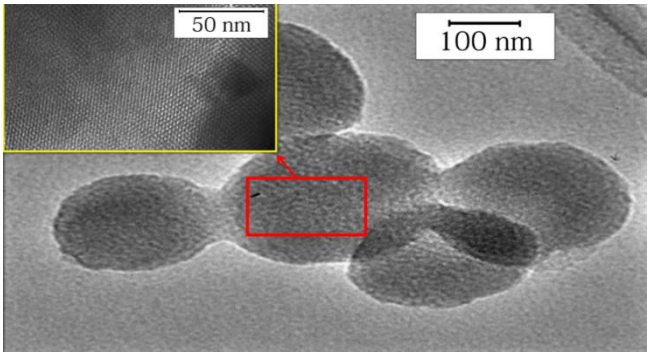

Figure 4. Transmission electron microscopy image of TMSPDETA/MCM-41.

3.2. Effect of contact time

The effect of contact time on the sorption of Pb (II) and Ni (II) ions onto the MCM-41/TMSPDETA nano hybrid adsorbent was indicated in Figure 5. As can be seen, a major portion of the total lead adsorption (i.e. more than 80%) was achieved within 10 min. The intial sorption rate of Ni (II) species has reached the equilibrium about 60 min after the beginning of stirring and remained constant until the end of the experimentation.

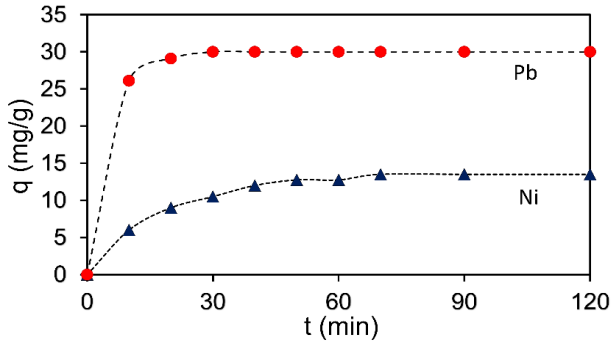

Figure 5. The effect of contact time on the uptake of Pb (II) and Ni (II).

3.3. Effect of temperature

In order to investigate the effect of temperature on the sorption capacity of Pb (II) and Ni (II) ions onto MCM-41/TMSPDETA nano hybrid adsorbent, the experiments were performed at different temperatures (20–50°C) and the temperature impact on Ni (II) sorption was less than Pb (II). The variation in the adsorption might have been the result of an increased tendency of Pb (II) and Ni (II) species to escape from the sorbent surface as the temperature of the solution rises [11]. Notably, for both cases the sorption capacity decreased with temperature and it was concluded that sorption of Pb (II) and Ni (II) species onto the MCM-41/TMSPDETA sorbent was an exothermic process.

3.4. Sorption kinetics

The experimental data were analyzed using three kinetic models including pseudo-first-order, pseudo-second-order and intraparticle diffusion.
Equations studied are defined as [12]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

$$q_t = k_{ipd} t^{1/2} + c \quad (4)$$

The parameters including rate constants k_1, k_2, k_{ipd}, c and correlation coefficients were calculated and the results are listed in Table 2.

This indicated that the pseudo-first order kinetic model coincided poorly to the adsorption processes of MCM-41/TMSPDETA for both Pb (II) and Ni (II) ions. However, in case of pseudo-second-order kinetic equation, the correlation coefficients were found to be greater than 0.99, and the corresponding equilibrium adsorption capacities fit well with the experimental data.

Table 1. $K_p$experimental permeability coefficients of each component at different temperatures [9, 10].

K_P: Permeability coefficient $g/(m^2 * h)$				
Temperature (K)	**Ethyl acetate**	**Water**	**ethanol**	**Acetic acid**
323	4963	260	1466	564
333	6495	340	1780	780
343	8157	470	2142	1029

The R^2 values of intraparticle diffusion model for both heavy metals were estimated much less than pseudo-second-order model which signified that diffusion was not the rate controlling step of the sorption process.

4. Conclusion

A novel MCM-41/TMSPDETA nano adsorbent was used for sorption of Ni (II) and Pb (II) ions from aqueous solutions. The FTIR spectra indicated that MCM-41/TMSPDETA nano adsorbent was functionalized by amine group. The kinetic data was best fitted by pseudo-second-order model kinetic with high regression coefficient (R^2>0.99). Contact time of 2h, temperature of 25°C and pH=6, respectively were optimum conditions determined for sorption process in a batch system.

References

[1] Freitas, O. M., Martins, R. J., Delerue-Matos, C. M., Boaventura, R. A. (2008). Removal of Cd (II), Zn (II) and Pb (II) from aqueous solutions by brown marine macro algae: kinetic modelling. *Journal of hazardous materials*, *153*(1), 493-501.

[2] Paulino, A. T., Santos, L. B., Nozaki, J. (2008). Removal of Pb 2+, Cu 2+, and Fe 3+ from battery manufacture wastewater by chitosan produced from silkworm chrysalides as a low-cost adsorbent. *Reactive and functional polymers*, *68*(2), 634-642.

[3] Mellah, A., Chegrouche, S., Barkat, M. (2007). The precipitation of ammonium uranyl carbonate (AUC): thermodynamic and kinetic investigations. *Hydrometallurgy*, *85*(2), 163-171.

[4] Kornilovich, B. Y., Koval'chuk, I. A., Pshinko, G. N., Tsapyuk, E. A., Krivoruchko, A. P. (2000). Water Treatment and Demineralization Technology-Water purification of uranium by the method of ultrafiltration. *Journal of Water chemistry and technology*, *22*(1), 43-47.

[5] Shoushtari, A. M., Zargaran, M., Abdouss, M. (2006). Preparation and characterization of high efficiency ion-exchange crosslinked acrylic fibers. *Journal of applied polymer science*, *101*(4), 2202-2209.

[6] de Pablo, L., Chávez, M. L., Abatal, M. (2011). Adsorption of heavy metals in acid to alkaline environments by montmorillonite and Ca-montmorillonite. *Chemical engineering journal*, *171*(3), 1276-1286.

[7] Babel, S., Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of hazardous materials*,*97*(1), 219-243.

[8] Hawari, A. H., Mulligan, C. N. (2006). Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass. *Bioresource technology*, *97*(4), 692-700.

[9] Zolfaghari, G., Esmaili-Sari, A., Anbia, M., Younesi, H., Amirmahmoodi, S., Ghafari-Nazari, A. (2011). Taguchi optimization approach for Pb (II) and Hg (II) removal from aqueous solutions using modified mesoporous carbon.*Journal of hazardous materials*, *192*(3), 1046-1055.

[10] Thomas, J. M. (1994). The chemistry of crystalline sponges. *Nature*, *368*(6469), 289-290.

[11] Zhou, L., Wang, Y., Liu, Z., Huang, Q. (2009). Characteristics of equilibrium, kinetics studies for adsorption of Hg (II), Cu (II), and Ni (II) ions by thiourea-modified magnetic chitosan microspheres. *Journal of hazardous materials*, *161*(2), 995-1002.

[12] Alkan, M., Demirbaş, Ö., Doğan, M. (2007). Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite. *Microporous and mesoporous materials*, *101*(3), 388-396.