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Research Article

Synthesis of NH_2-MCM-41 Nano Porous Adsorbent and Using it for Zn and Ag Metals Removal from Aqueous Solutions by Adsorption Method and Studying Effect of Some Physicochemical Parameters on it

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Abstract: In this study we have investigated removal of Zn and Ag Ions from aqueous solutions. Industrial pollutions by heavy metals ions as Ag and Zn is a universal environmental problem, because of their toxicity. Thus, we have studied removal of these ions by NH_2-MCM-41 nano porous adsorbent at room temperature. This adsorbent has a high surface area, high adsorption ability, high factor of porosity and wide porous. In the batch experiment we have taken 150 cm^{-3} of considered metallic ion aqueous solution. After pH adjustment, nano porous absorbent was added and it was agitated by a rotary shaker. Then, pH, amount of adsorbent, initial concentration of metallic ion, time of contact and temperature parameters have determined. Thus, recovery of Ag and Zn metallic ions at pH = 7, adsorbent dose of 2 g/dm^3 and room temperature obtained 96.93 and 99.24%, respectively. Thermodynamic results indicate that adsorption process is endothermic and spontaneous. Obtained adsorption isotherm was fitted by Langmuir's adsorption isotherm which is single-layer adsorption. Moreover, this removal process has a second order kinetic. Synthesized adsorbent was characterized by FT-IR, SEM and XRD.

Keywords: Langmuir's isotherm, mesoporous adsorbents, nano porous, NH_2-MCM-41

INTRODUCTION

Development of Chemical, Wooden, textile, insecticides and drug industries were introduced necessarily, a series of pollutants into environmental extent which will increase continuously (Norton *et al.*, 2004). In an approach, clinopetilolite (a natural zeolite) was used for removal of Ag ions in aqueous solutions (Murat *et al.*, 2006). In this investigation, the reaction between Ag^+ and zeolite was studied. The results show that some factors as pH, contact time, concentration and acidic behavior of Ag^+, affect adsorption process.

Removal of Zn, Cu, Ni, Ag and Cr was experimented by aluminum electro coagulation and hydrolysis mechanism, precipitation and hydroxidizing of these metallic ions was studied (Heidman and Calmano, 2008). Removal of metallic ions also was examined by biological adsorption (Chen and Wang, 2008) which may be defined by quasi second order kinetic. Removals of Ag was studied by adsorption on synthetic chelating polymer in continuous and discontinuous systems (Abd El-Ghaffar *et al.*, 2009) which have shown the process is endothermic and have a second order kinetic.

Also, other investigations was performed as, adsorption of Zn^{2+} from aqueous solutions (Kwon *et al.*, 2005), separation of Ag^+ and Cu^{2+} from binary solution based on Hard-Soft Acid Base theory (HSAB) (Lam *et al.*, 2005), selective removal of Cd^{2+} and Zn^{2+} from aqueous solutions by modified clinopetilolite (Hajialigol *et al.*, 2006), removal of heavy metals from aqueous solutions by adsorption on brown alga (Freitas *et al.*, 2008), removal of Zn^{2+} by using hybrid precursor of silicon and carbon (Gupta *et al.*, 2010), removal of Zn^{2+} by using Moringa Oleifera Lam (Bhatti *et al.*, 2007), adsorption of Zn^{2+} by modified mesoporous silicate MCM-41 (Sepehrian *et al.*, 2009), removal of Ni^{2+}, Cd^{2+} and Pb^{2+} from ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica (Heidari *et al.*, 2009).

Non selective adsorbents as activated carbon, clays, ion exchange resins and silica have some problems as adsorption capability, low selectivity, high adsorption time, thermal and mechanical instability (Monteagudo and Ortiz, 2000).

Recently, in different domains such as chemical engineering, biological dissociation and environmental refining, selective adsorption method was discussed. In this process subjected ion will remove selectively either from gas or from by adsorption, this process based on physical and chemical properties of subjected ion (Jal *et al.*, 2004; Chwastowska *et al.*, 1999). Effect of selective adsorbents is due to formation of chemical complex between metallic ion and functional group over the surface of adsorbent. Recently, mesoporous silica have much more interested because of their large

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surface area, shape and size of porous and modifiable surface properties (Perez-Quintanilla *et al*., 2006; Yoshitake *et al*., 2003). Chemical modifying of surface of these mesoporous materials by bonding silanol and several functional groups results in formation of hybrid materials and these organic-inorganic hybrid materials have high capability of adsorption of heavy metals ions (Mureseanu *et al*., 2004). Many mesoporous silica were functionalized by different ligands and are used for removing heavy metals from waste water. SAB-15 (Santa Barbara Amorphous no-15) functionalized by amine groups shows bonding ability with Cu^{2+}, Zn^{2+}, Cr^{2+} and Ni^{2+} metallic ions and removal them from aqueous solutions (Bois *et al*., 2005).

In this study we have used NH_2-MCM-41 as inorganic adsorbent for Ag^+ and Zn^{2+} removal from aqueous solutions in non continuous system.

MATERIALS AND METHODS

This Study was performed as a research project in Payame Noor University in department of Chemistry of Sari center in 2011-2012.

Materials: All materials used in this investigation are of analytical grade from Merck Company (Germany).

Instruments: XRD analysis are performed by *X'* pert Philips Holland model by voltage intensity of 40 kV and K_αCu irradiation ($\lambda = 1.54$ Å).

Shape and size of synthesis materials have evaluated by Scanning Electronic Microscopy (SEM), SEM Philips *XL30*, Holland model.

IR spectrophotometer was performed by Schimadzo FT-IR1650 Spectrophotometer Japan model in wave length range 400-4000 cm^{-1}.

Incubator-shaker Jaltahis JTFL-2 model.

Methods and experiments: MCM-41, NH_2-MCM-41 were synthesized and ion metallic solutions was prepared by following methods:

Synthesis of MCM-41: (0.64 g) (0.0163 mol) sodium hydroxide was dissolved in 27 mL of deionized water. Then 1.8 g (0.30 mol) silicon oxide was added at 80°C within an interval of 3 h for complete dissolving. After cooling this solution in room temperature, 5.64 g (0.015 mol) hexa-acetyl three methyl Ammonium Bromide (CTAB) was added at room temperature under rough agitating condition and a homogenous and viscous solution was obtained. (0.3 mL) (0.0102 mol) hydrochloric acid was added after 1 h, also, 24 mL deionized water was added after 10 m and then obtained gel was supported a rough agitation for 2 h. This mixed gel, then, was placed in a Teflon vessel and sustain 3 days in an oven at 100°C. This solution was cooled to room temperature and filtered by an ordinary filter. Obtained solid substance was rinsed a few times by deionizer water and dried 10 h at 100°C. The obtained white powder was calcified in two steps, firstly, for 2 h in 150°C, secondly, temperature was increased with a rate of 3°C/min to 540°C and remained at this temperature for 6 h and then it was cooled to room temperature in a desiccator.

Synthesis of NH_2-MCM-41: Two and half gram above prepared MCM-41 and 50 mL n-hexane was placed in a heating flask and then 2.5 g 3-aminopropyle three metoxy silane was added to it. This mixture was refluxed 6 h and after cooling to room temperature it was filtered and washed slowly by 20 mL n-hexane.

The obtained NH_2-MCM-41 must be preserve in a desiccators containing moisture absorbent material.

Providing ion metallic solutions: In this study, it was provided ion metallic solutions with a concentration of 1000 mg/L (1000 ppm). $AgNO_3$ and $ZnCl_2$ were used for preparing Ag^+ and Zn^{2+} solutions, respectively.

Adsorption tests in non continuous system: Experiments were performed by nano porous adsorbents MCM-41 and NH_2-MCM-41 in non continuous system. Effect of pH, amount of adsorbent, initial concentration of metallic ion, contact time and temperature parameters was studied by variation one of these parameters and stabilizing the others. Firstly, the optimize pH and amount of adsorbent was determined when equilibrium achieves, then by using these optimized parameters other parameters was optimized. Thus optimized parameters for adsorption as pH = 7, amount of adsorbent equal to 2 g/L and initial concentration of metallic ion equal to 200 mg/L was determined in temperature range of 5 to 45°C.

Data analyzing in non continuous system: Adsorption capacity q (mg/g) of Ag^+ and Zn^{2+} ions by synthesized adsorbent was calculated as:

$$q = \frac{(C_o - C_e)V}{W} \tag{1}$$

where,

q = Metallic ion adsorption (mg/g)
V = The volume of concentration (mL)
C_o = Initial concentration of metallic ion (mg/L)
C_e = Final concentration of metallic ion (mg/L)
W = The weight of adsorbent (g)

The value of ion metallic removal *R* was calculated as:

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

where, *R%* is the percentage of metallic ion adsorption by adsorbent. The calculation of *q* and *R%* was performed by Microsoft Excel software. Also for kinetic study calculation following equation was used:

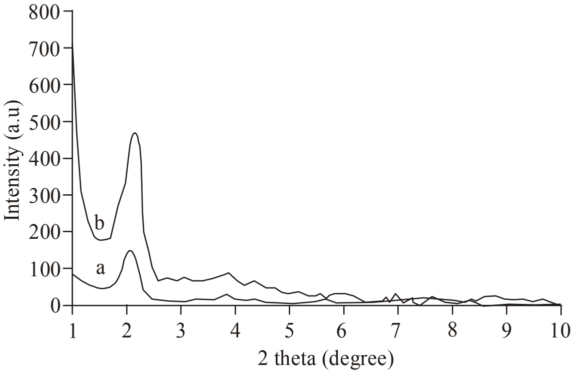


Fig. 1: XRD spectra of mesoporous adsorbents (a) NH_2-MCM-41, (b) MCM-41

$$q_t = \frac{(C_o - C_t)V}{W} \tag{3}$$

where,

q_t : Capacity of adsorption of metallic ion (mg/g) in time t

C_t : The concentration of metallic ion in solution (mg/L) in time t

For calculation of the value of desorption following equation was used:

$$D\% = \frac{C_t V}{W} \times 100 \tag{4}$$

where, $D\%$ is the percentage of desorption (Hartinger, 1994).

RESULTS AND DISCUSSION

XRD spectra: Figure 1 shows XRD spectra of NH_2-MCM-41 and MCM-41. There is a sharp peak in $2\theta = 2.09$ which may be attributed to diffraction of (100) plane of hexagonal structure. Moreover, weak intensity peaks can be observed which is attributed to (200) and (110) diffractions and confirm formation of the porous having hexagonal structure with high order.

FT-IR spectra: FT-IR spectra of NH_2-MCM-41 and MCM-41 mesoporous adsorbent are shown in Fig. 2. The peaks observed in MCM-41 spectrum in 1560 and 1650 cm^{-1} are in relation with amine groups. The large and extended bond in 3055-3760 cm^{-1} is due to reaction of Si-OH groups with adsorbed molecules of water and destructed sites. Si-O-Si vibrations peaks observed in 1095 cm^{-1} is in relation with asymmetric tension, in 814 cm^{-1} is in relation with symmetric tension and in 460 cm^{-1} is due to flexible tension.

On NH_2-MCM-41 spectrum (Fig. 2) a large bond can be observed in 1560 cm^{-1} which is due to flexible tension of N-H Group. It may be noted that tensional bond of N-H in 3200-3500 cm^{-1} and tensional bond of C-N in 1030-1230 cm^{-1} is overlapped with large bond of silanol and Si-O-Si vibrations.

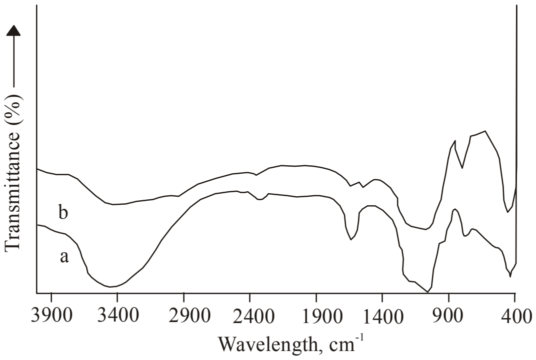


Fig. 2: FT-IR spectra of mesoporous adsorbents (a) NH_2-MCM-41, (b) MCM-41

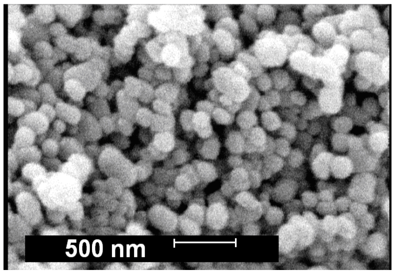


Fig. 3: SEM image of mesoporous MCM-41

SEM image of MCM-41 mesoporous particles: Figure 3 shows SEM image of MCM-41. This image shows the general morphology of particles and indicates this fact, the spherical particles of mesoporous MCM-41 was formed. Since this image was taken after calcifying, thus indicates stability of structure and retaining its morphology during calcifying treatment. Distribution of particles as observe on SEM image shows that the size of particles is between 60 to 80 nm.

Effect of pH on adsorption of Ag^+ and Zn^{2+} by mesoporous adsorbent NH_2-MCM-41: pH of aqueous solutions is most important parameter in adsorption process, because affects ion metallic solubility, number of ions on functional group surface of adsorbent and the degree of ionization during reaction. Characteristics of adsorbent and adsorbed vary by variation of pH. Functional groups of NH_2-MCM-41 adsorbent are much more affected by pH of solution (Cai *et al.*, 2001). Figure 4 shows the results of pH effect on adsorption yield Ag^+ and Zn^{2+}. In this study, initial concentration of metallic ions was 100 mg/L. Adsorptions of Ag^+ and Zn^{2+} were studied in pH = 4, 5, 6, 7, 8, 9 and in pH = 3, 4, 5, 6, 7, respectively. Since the removal of ions in the pHs lower than 4 is small and in pHs higher than 9 for Ag^+ and higher than 7 for Zn^{2+} because of high concentration of OH^- ions metallic ions

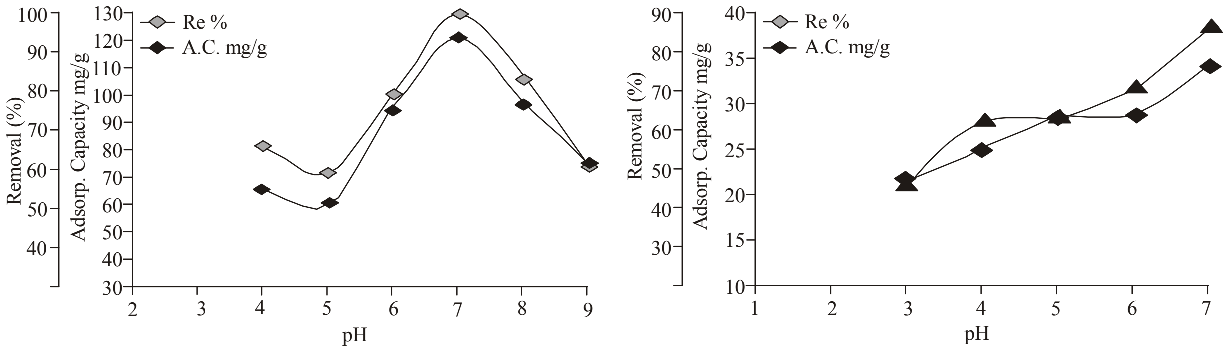


Fig. 4: Effect of pH on adsorption of (a) Ag^+, (b) Zn^{2+} On NH_2-MCM-41adsorbent. Initial concentration of ions is 100 mg/L and concentration of adsorbent is 0.75 g/L for Ag^+ and 1.50 g/L for Zn^{2+}

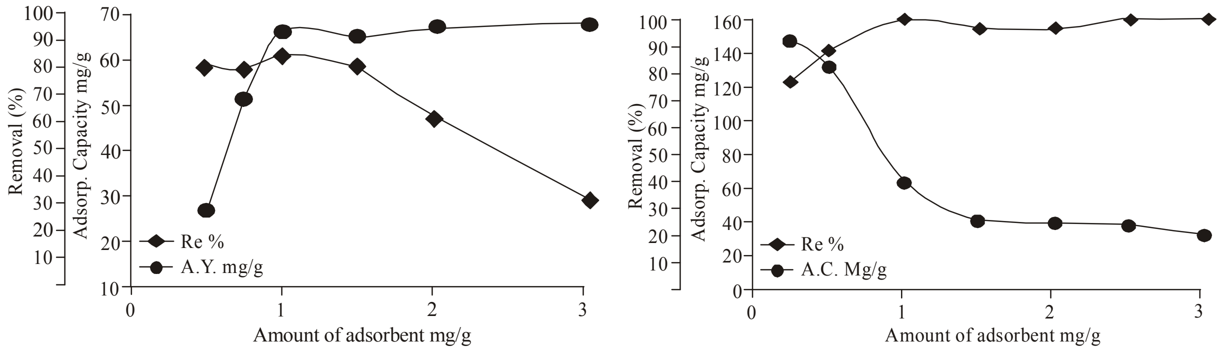


Fig. 5: Effect of amount of NH_2-MCM-41adsorbent on adsorption of (a) Ag^+, (b) Zn^{2+}. Initial concentration of metallic ion is 100 mg/L and pH = 7

precipitate as hydroxides and thus the range of 4-9 for Ag^+ and 3-7 for Zn^{2+} was selected.

These results show that in low pHs, existent amine group on the surface of adsorbent was protonated and lose its ability as a complexing ligand for metallic ions.

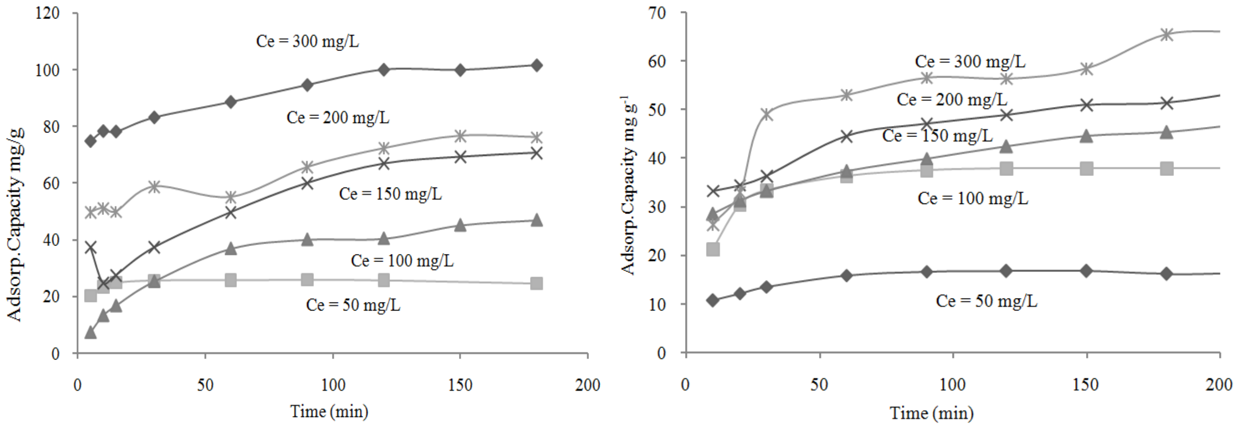
Effect of amount of adsorbent on metallic ions adsorption: The amount of adsorbent is an important parameter which determines capacity of adsorption for a given initial concentration of metallic ions. Figure 5 shows the effect of amount of adsorbent on Ag^+ and Zn^{2+} adsorption.

Increasing the amount of adsorbent, also removal of Ag^+ and Zn^{2+} will increase. This is because of surface area increasing of mesoporous adsorbent and thus active sites for complexing metallic ions will increase and adsorption process also, will increase. Figure 5 shows evidently that increase of adsorbent's amount will increase removal of Ag^+ to 97.95% and removal of Zn^{2+} to 100%. This indicates that increasing the amount of adsorbent, available sites on surface area also, will increase

Effect of initial concentration of metallic ion: The experiments for determining the effect of concentration of Ag^+ and Zn^{2+} on their removal by NH_2-MCM-41 adsorbent was performed at pH = 7, concentration of adsorbent 2 mg/g and initial concentration range of metallic ions 50 to 300 mg/L. The results of this study were shown on Fig. 6.

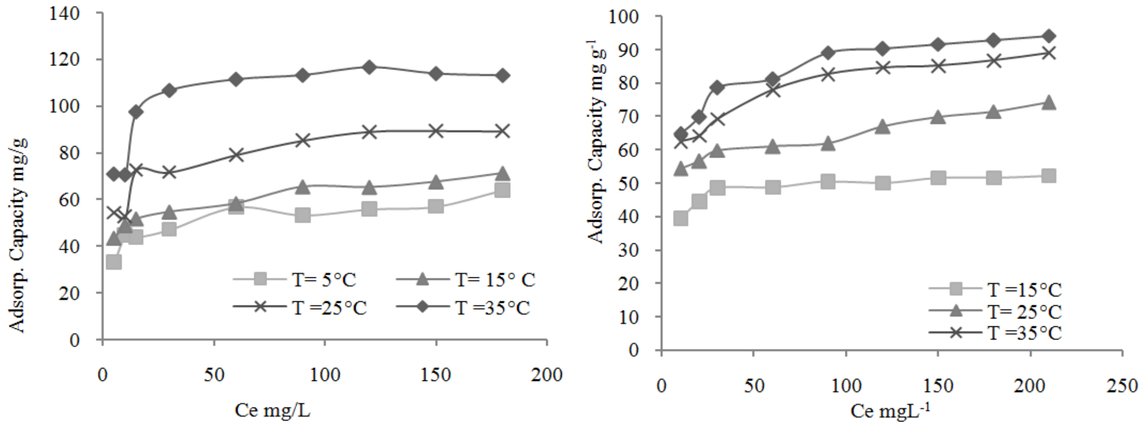
The results show that maximum removal occurs at minimum concentration. Increasing in concentration of metallic ions will decrease removal yield. However, increasing initial concentration of metallic ion decreases its removal from aqueous solution, but increases its adsorption capacity of adsorbent. This may be interpreted by this fact that, in lower initial concentration of metallic ions adsorbent isn't, however, saturated by these ions.

By increase of initial concentration of metallic ions, the number of ions for reacting with active amine groups increases, resulting in saturation of active sites on adsorbent surface. In other words, adsorption capacity of adsorbent will increase by increase of metallic ions in aqueous solution. Moreover, increase of metallic ions increase the contacts between these ions with adsorbent surface and result in increase of adsorption process rate. Increasing initial concentration of metallic ion in solution, also, leads to electrostatic reaction increasing which provides the sites with smaller reactivity for reaction. As it may be deduced from Fig. 6, adsorption capacity for initial concentration of 300 mg/L of metallic ions, arises to 101.45 mg/L (94.32%) for Ag^+ and to 66.02 mg/g for Zn^{2+} (77.45%) which is due to rapid saturation of adsorbent.



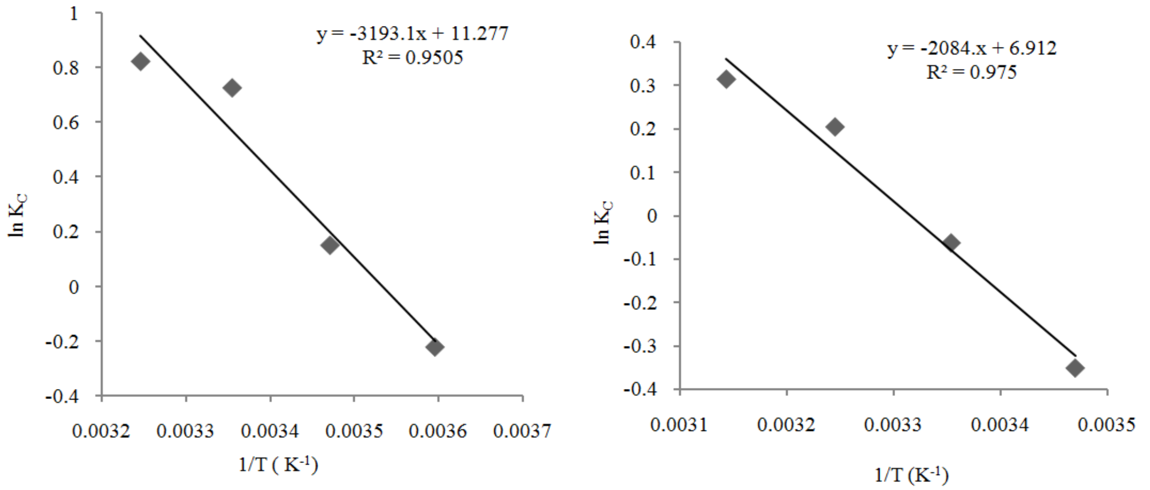
(a) (b)

Fig. 6: Effect of initial concentration (Ce) on adsorption of (a) Ag^+, (b) Zn^{2+}. Concentration of NH_2-MCM-41 adsorbent is 2 mg/g and pH = 7



(a) (b)

Fig. 7: Effect of temperature on adsorption of (a) Ag^+, (b) Zn^{2+} by NH_2-MCM-41 adsorbent. Concentration of NH_2-MCM-41 adsorbent is 2 mg/g, pH = 7 and Initial concentration of metallic ion is 200 mg/L



(a) (b)

Fig. 8: Vant ln K_C against 1/T plot for adsorption of (a) Ag^+, (b) Zn^{2+} by NH_2-MCM-41 adsorbent. Concentration of NH_2-MCM-41 adsorbent is 2 mg/g, pH = 7 and Initial concentration of metallic ion is 200 mg/L

Table 1: Thermodynamic parameters for adsorption of Ag^+ and Zn^{2+} by NH_2-MCM-41 adsorbent at different temperatures

Ion	mg/L	ΔH° (J/moL)	ΔS° (J/moL)	ΔG° (J/moL)			
Ag^+	200	61136.82	215.79	278 K	288 K	298 K	308 K
				1149.98	-1007.82	-3165.42	-5303.40
Zn^{2+}	200	39902.64	132.34	288 K	298 K	308 K	318 K
				3112.12	1788.72	-858.08	-2181.72

Effect of temperature and thermodynamic study: Temperature has a significant and conclusive effect on adsorption ability of adsorbent. Experiences show that by increase of temperature adsorption of metallic ions will increase which indicates the process is endothermic. This may be interpreted as, increase in temperature increases collision frequency and also high temperature may be raise either dimensions of porous or activation energy. Figure 7 shows the effect of temperature on adsorption of Ag^+ and Zn^{2+} by NH_2-MCM-41 adsorbent.

Studying these reactions thermodynamically, K_C was obtained at 278.15, 288.15, 298.15 and 308.15 K for Ag^+ and at 288.15, 298.15, 308.15 and 318.15 K for Zn^{2+}, respectively. Then the plots of ln KC against 1/T adsorption reaction were traced. Figure 8 shows the plot of ln K_C against 1/T for these reactions.

ΔH° and ΔS° were obtained from slopes and intercepts of plots, respectively. ΔG°, also, may be calculated from $\Delta G° = \Delta H° - T\Delta S°$ equation. Determined values of ΔH° and ΔS° and calculated value of ΔG^o are reported in Table 1.

From Table 1, it can be observed that enthalpy, entropy and Gibbs free energy of these processes are positive at 273.15 K which indicates endothermic characteristic of adsorption process and high efficiency of this adsorbent for Ag^+ and Zn^{2+}. But, as it can be deduced from Table 1, at higher temperature (ambient temperature), Gibbs free energy turns to be negative and this indicates spontaneous behavior of process. Positive value of entropy shows increase of disorder throughout the surface during adsorption process.

CONCLUSION

In this study it was shown usefulness of nanotechnology in removal of heavy metal ions from aqueous milieu in a non continuous system. Considering the risks of toxicity of heavy metals even in small quantities, their adsorption by mesoporous NH_2-MCM-41 adsorbent will have a remarkable importance. The results show that, pH, amount of adsorbent, initial concentration of metallic ion and temperature variation have an operative effect on adsorption process.

Increasing these parameters will increase adsorption capacity of adsorbent. Optimized values for first three parameters were obtained as, pH = 7, amount of adsorbent = 2 mg/g and initial concentration of metallic ion = 300 mg/L.

Temperature variations and thermodynamic study show that ΔH°, ΔS° and ΔG° have positive values at 273.15 K which indicates endothermic character of adsorption process in this temperature. But in ambient temperature ΔG° becomes negative which indicates spontaneous characteristic of this process in higher temperatures. Positive value of ΔS° shows increase of disorder by temperature increasing.

At last, this investigation shows that mesoporous NH_2-MCM-4 is a suitable adsorbent for removal of toxic metallic ions and it may be possible, also, to remove these ions from waste water.

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