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Studying Kinetics and Isothermal equilibrium of Synthesized NH_2 – MCM – 41 Nano Mesoporous Adsorbent

F. Ashrafi[1]*, N. Jamshidi Ghadikolaei[1], A. Javidan[2]

[1]Payame Noor University, Dept. of Chemistry, P.O. Box19395-3697, Tehran, Iran
[2]Politecnico di Torino, Torino, Italy.

***Corres. author: ashrafifer@yahoo.com**

Abstract: In this study we have discussed kinetics data and isotherm equilibrium analyses obtained as results from adsorption of Ag and Zn ions by synthesized NH_2 – MCM – 41 nano mesoporous adsorbent. Kinetics studies of this adsorbent having much importance in its adsorption behavior because of providing the data on reaction conditions and also define controlled rate of adsorption of solution. Determining the rate of metallic ions' adsorption, linear form of pseudo-first order and pseudo-second order models were used. The plots traced from kinetics data have more accordance with pseudo-second order model. On the other hand, isotherm equilibrium analyses are used for determining adsorption behavior of Ag and Zn ions in solution byNH_2 – MCM – 41 nano mesoporous adsorbent. For this purpose we have discussed Langmuir, Freundlich and Temkin adsorption isotherms on the base of experimental data.
Keywords: Nano mesoporous adsorbent, pseudo-second order, pseudo-second order, Langmuir isotherm, Freundlich isotherm, Temkinisotherm.

Introduction

Studies on synthesizing NH_2 – MCM – 41 nano mesoporous adsorbent have performed recently[1].In this work, kinetics of adsorption and isothermal behavior of synthesized NH2 – MCM – 41 nano mesoporous adsorbent were investigated. Equilibrium and kinetics of adsorption and analyzing the results have been discussed by several authors.Douong's book covers topics of equilibria and kinetics of adsorption in porous media. Fundamental equilibria and kinetics are dealt with for homogeneous as well as heterogeneous particles. In kinetics analysis, it deals with the various mass transport processes and their interactions inside a porous particle[2].

The kinetics of sorption from a solution onto an adsorbent has been explored theoretically. It has been shown that at high initial concentration of solute the general equation converts to a pseudo-first-order model and at lower initial concentration of solute it converts to a pseudo-second-order model[3]. Investigation on kinetics and equilibrium of removal of copper and zinc ions from aqueous effluents by bone char has been studied in single component sorption systems. The equilibrium isotherms are best described by a Langmuir–Freundlich (L–F) type isotherm equation. The kinetics of sorption of the two metal ions has been analyzed by two kinetic models, namely, the Lagergren pseudo first-order model and the Elovich kinetic model. The Elovich equation provides the best fit to experimental data[4]. Kinetics and equilibrium of adsorption were studied for

several metal ions, namely, Pb2+, Cu2+, Zn2+, Cd2+, and Ni2+ cations. In this study the kinetic parameters of the models were calculated and discussed.For an 8 × 10-4 M initial metal concentration, the initial sorption rates (v0) ranged from 0.063 mmol·g-1·min-1 for Pb2+ to 0.275 mmol·g-1·min-1 for Ni2+ ions, in the order Ni2+ > Cd2+ > Zn2+ > Cu2+ > Pb2+. The equilibrium data fitted well with the Langmuir and Freundlich models and showed the following affinity order of the material: Pb2+> Cu2+> Zn2+ > Cd2+ > Ni2+[5]. The sorption of lead ions onto peat has been studied.

Equilibrium isotherms have been measured and modeled. Kinetic studies have been carried out in a batch adsorbent to study the effect of initial concentration, agitation and temperature. A pseudo-second order kinetic model has been proposed to correlate the experimental data[6]. A literature review of the use of sorbents and biosorbents to treat polluted aqueous effluents containing dyes/organics or metal ions have been conducted. Over 70 systems have been a pseudo-first order kinetic mechanism. Three sorption kinetic models which are presented have been used to test as first order kinetics and one system as a second order process. In all these systems, the highest correlation coefficients were obtained for the pseudo-second order kinetic model[7]. A recent investigation studied influence of two experimental parameters, initial 18-crown-6 concentration and temperature, on the adsorption kinetics was evaluated. The kinetics data obtained were modeled by pseudo-first-order and pseudo-second-order models, respectively. The process of adsorption follows a pseudo-second-order rate model[8]. Adsorption of malachite green (MG) was studied using three adsorbents namely, bagasse fly ash (BFA), a sugar industry waste, and activated carbons commercial grade (ACC) and laboratory grade (ACL). The adsorption followed pseudo-second-order kinetics. Equilibrium adsorption data on BFA, ACC and ACL were analyzed by Freundlich, Langmuir, Dubnin–Radushkevich, Redlich–Peterson and Temkin isotherm equations using regression analysis. Non-linear error analysis showed that the Freundlich isotherm best-fits the equilibrium data for adsorptive removal of MG by BFA and ACC and Redlich–Peterson best follows the equilibrium data for ACL[9]. A study used distillation waste of rose petals was to remove Cu (II) and Cr (III) from aqueous solutions. The obtained results show that the Freundlich regression model and pseudo-second-order kinetic model were resulted in high correlation coefficients and described well the sorption of Cu(II) and Cr(III) on rose waste biomass[10]. The sorption of platinum by immobilized Saccharomyces cerevisiae biomass was observed to be a chemical sorption mechanism (second order), with rapid initial sorption resulting in removal of approximately 70% of the metal from a 50 mg/l platinum solution in 5minutes.

The mechanism of the sorption also influences the kinetics, by the first-order physical sorption mechanisms allowing rapid establishment of equilibrium conditions, while the second-order chemical mechanisms result in slow kinetics with equilibrium establishment taking as long as 24–48 h to occur[11]. In this paper we will discuss the results of kinetic study of adsorption of Ag and Zn metallic ions byNH2 – MCM – 41 nano mesoporous adsorbent. Also, for better prediction of adsorption behavior of these ions, Langmuir, Freundlich and Temkin isotherms were used.

Materials and Methods

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

Methods: Synthesizing nano mesoporousNH2 – MCM – 41, was performed by the same method as carried out in [1], i.e. 2.5 of MCM-41 and 50 mL n-hexane was placed in a heating flask and then 2.5 g 3-aminopropyle three methoxy silane was added to this flask. This mixture was refluxed 6 hours and after cooling to room temperature it was filtered and washed slowly by 20 mL n-hexane. The obtained nano NH_2-MCM-41 was preserved in a desiccator containing moisture absorbent material.

Ion metallic solutions were provided by a concentration of 1000 mg L^{-1} (1000 ppm). $AgNO_3$ and $ZnCl_2$ were used for preparing Ag^+ and Zn^{2+} solutions, respectively.

Kinetic study of adsorption: Kinetic studies were performed on 50, 100, 150, 200, 250 and 300 mg L^{-1} of both ion metallic solutions. The experiments were carried out from zero to 300 minutes.

Results and discussion

Adsorption kinetics study: Here we will study and discuss the experimental data of equilibrium and kinetics of silver and zinc metallic ions adsorption by NH_2 – MCM – 41 nano mesoporous adsorbent. Pseudo-first order

model is used for studying reversible reactions which are established between the liquid and solid phases, while, pseudo-second order model assume that the rate-limiting step may be as chemisorption. Considering obtained results based on calculative and experimental data, which are indicated in table 1 and table 2, pseudo-second order is more convenient with kinetic data in both cases.

Pseudo-first order plots were shown in figure 1. The plots were traced using following equation:

$$ln(q_e - q_t) = -k_1 t \qquad (1)$$

Where q_e and q_t are the amounts of adsorbed substance by mass unit of adsorbent and k_1 is the constant rate of pseudo-first order adsorption. The obtained data for first order kinetics have significant deviation from experimental values in both cases. Calculated values of $q_e$have much difference with experimental data and the values of R^2 are not acceptable both cases of adsorption. So that, first-order kinetics can't be suitable for these cases.

The calculated values for second-order kinetics show more convenient with experimental data which were obtained from plots. The plots were traced using following equation:

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

Where k2 is the constant rate of pseudo-second order adsorption. Calculated values of qe are close to experimental data and the values of R2 are almost suitable. Consequently, suggested model of pseudo-second order kinetics may be much more convenient with the adsorption of Ag and Zn by nano mesoporous NH2 – MCM – 41 adsorbent.

Table 1.Resulting data of pseudo-first order and pseudo-second order kinetic constants at different concentration of silver ions.

Initial concentration of Ag^+ mg.g^{-1}	Pseudo-first order model			q_e Experimental mg.g-1	Pseudo-second order model		
	$k_1\times10^{-2}$ 1.min^{-1}	q_e Calculated mg.g^{-1}	R^2		$k_2\times10^{-3}$ g.mg^{-1}.min^{-1}	q_e Calculated mg.g^{-1}	R^2
50	37.5	83.88	0.969	24.6	15.7	22.72	0.962
100	1.84	39.99	0.955	46.86	0.54	55.56	0.966
150	2.00	54.57	0.947	70.63	0.47	83.33	0.982
200	0.46	23.22	0.199	76.16	0.21	71.43	0.978
250	1.15	59.84	0.543	87.26	0.30	111.11	0.964
300	2.00	32.58	0.941	101.45	1.60	111.11	0.998

Table 2. Resulting data of pseudo-first order and pseudo-second order kinetic constants at different concentration of Zinc ions.

Initial concentration of Zn^{2+} mg.g^{-1}	Pseudo-first order model			q_e Experimental mg.g-1	Pseudo-second order model		
	$k_1\times10^{-2}$ 1.min^{-1}	q_e Calculated mg.g^{-1}	R^2		$k_2\times10^{-3}$ g.mg^{-1}.min^{-1}	q_e Calculated mg.g^{-1}	R^2
50	1.15	3.22	0.414	16.42	12.5	16.39	0.986
100	2.53	6.50	0.566	37.96	4.00	40.00	0.999
150	1.38	22.54	0.992	47.15	1.40	50.00	0.995
200	0.23	3.73	0.057	53.83	1.20	58.82	0.997
250	1.61	31.62	0.930	56.65	0.10	62.50	0.993
300	1.61	45.50	0.834	77.74	0.70	71.43	0.991

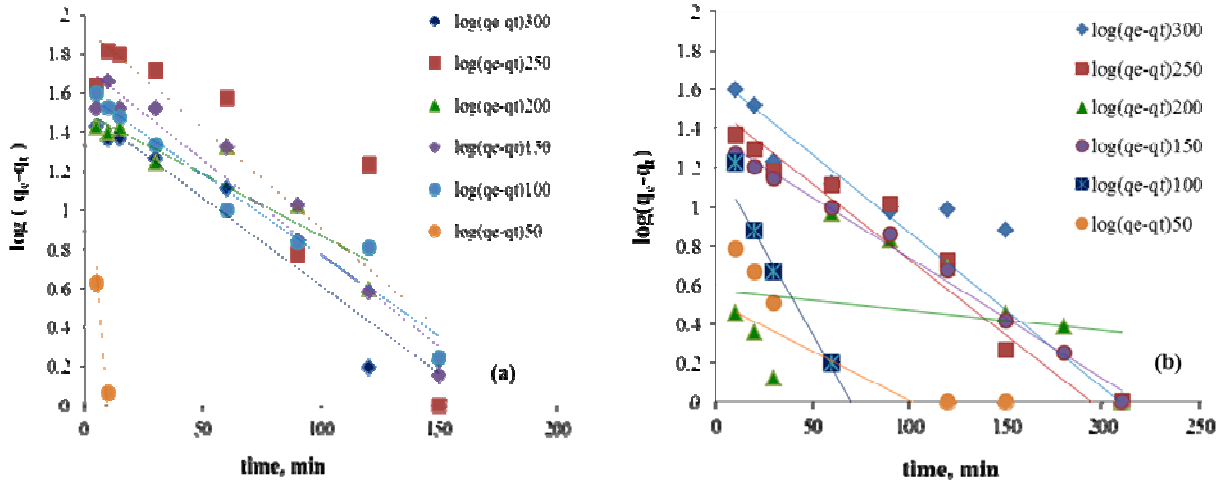

Figure 1. Pseudo-first order plots of (a) Ag and (b) Zn adsorption by NH2-MCM-41. Amount of adsorbent 2 g L^{-1}, pH = 7, initial concentration 200 mg L^{-1}

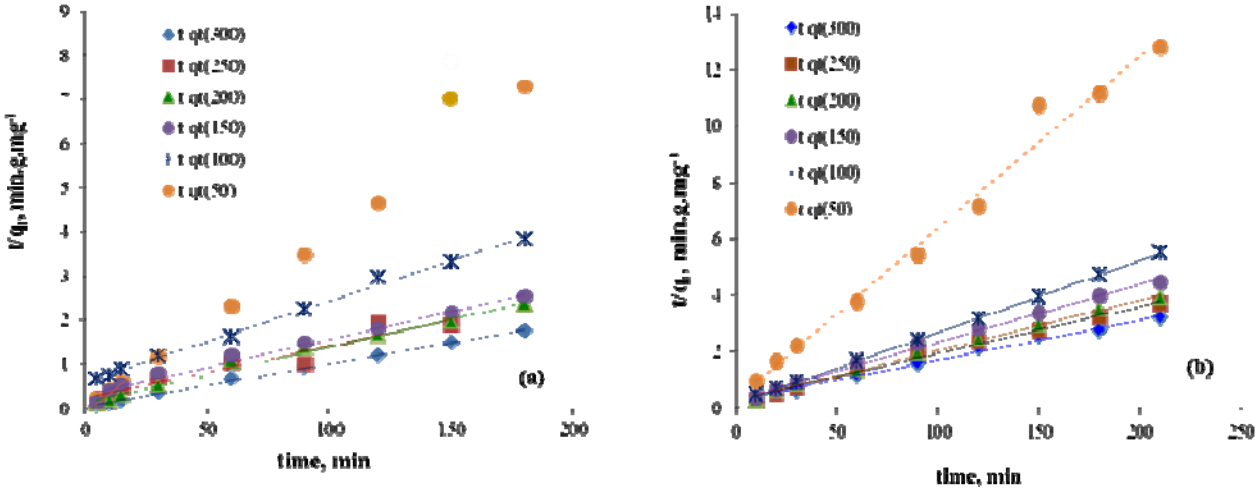

Figure 2. Pseudo-second order plots of (a) Ag and (b) Zn adsorption by NH2-MCM-41. Amount of adsorbent 2 g L-1, pH = 7, initial concentration 200 mg L-1

Adsorption equilibrium studies: With a view to adsorption behavior of Ag and Zn ions in solution by nano mesoporous NH2 – MCM – 41 adsorbent, Langmuir, Freundlich and Temkin isotherms were studied. Langmuir model was used for determination of maximum capacity of adsorption. For studying this model, linear form of Langmuir's equation was given as:

$$\frac{p}{q_e} = \frac{1}{q_m K_L} + \frac{p}{q_m} \qquad (3)$$

Where q_m is maximum adsorption of metal over the surface of adsorbent, i.e. saturation of adsorbent sites for adsorption,$K_L$is Langmuir constant which is in relation with adsorption enthalpy and $q_e$is the amount of adsorption at equilibrium. Separating factor R_L, which will indicate Langmuir isotherm is either acceptable or non-acceptable in present case, has given as:

$$R_L = \frac{1}{1 + bC_o} \qquad (4)$$

Where C_o is initial concentration and b is Langmuir's constant.

Freundlich isotherm model is essentially based on experimental data and was used for adsorption over heterogeneous surfaces or the surfaces which give the sites with different tendency of adsorption and was used widely for comparing experimental data. Linear form of Freundlich equation gives as:

$$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e \qquad (5)$$

Where K_F is Freundlich constant which used as a relative measure of biosorption capacity, n is another Freundlich constant which indicates intensity of adsorption and C_e is concentration at equilibrium.

Temkin isotherm model depends to some interaction effects on adsorption isotherms. These effects are due to repulsion forces over a homogeneous or heterogeneous surface. Temkin isotherm equation gives as:

$$q_e = \frac{RT}{b} ln\, AC_e \qquad (6)$$

Where b and A are Temkin constants.

Figures 3, 4 and 5 show the plots of Langmuir, Freundlich and Temkin isotherms adsorption process by nano mesoporous NH2 – MCM – 41 adsorbent, respectively. The plots were traced by using linear form of above equations. Using linear calibration method and the results obtained from plots it may be deduced that which isotherm follows adsorption and obtained results are indicated in table 3.

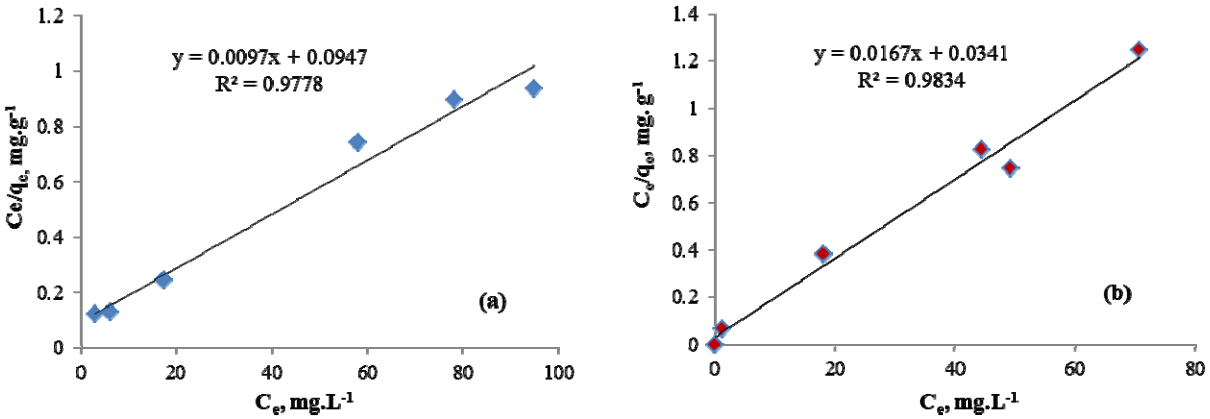

Figure 3. The plots of Langmuir isotherm for adsorption of (a) Ag and (b) Zn ions over NH2 – MCM – 41. Amount of adsorbent 2 g L-1, pH = 7, initial concentration 200 mg L-1

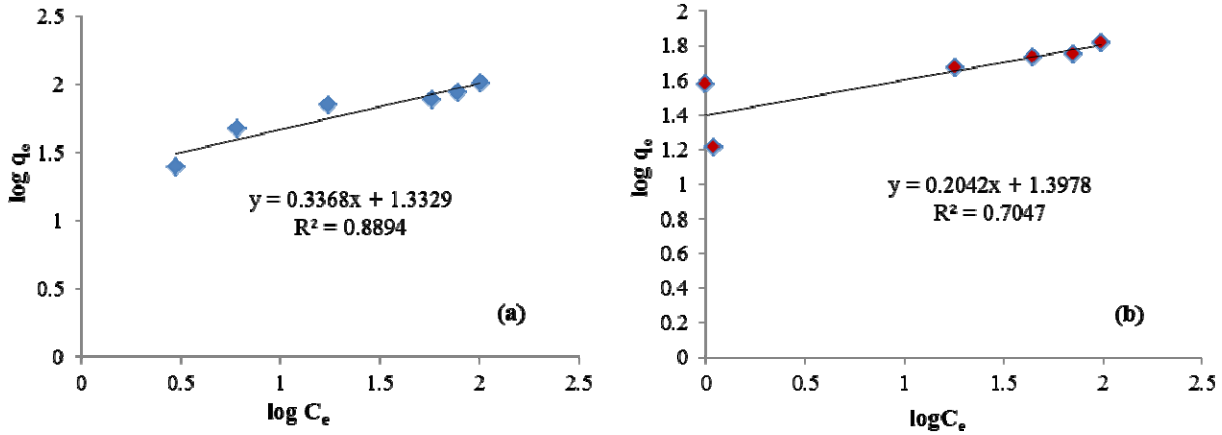

Figure 4. The plots of Freundlich isotherm for adsorption of (a) Ag and (b) Zn ions over NH2 – MCM – 41. Amount of adsorbent 2 g L-1, pH = 7, initial concentration 200 mg L-1

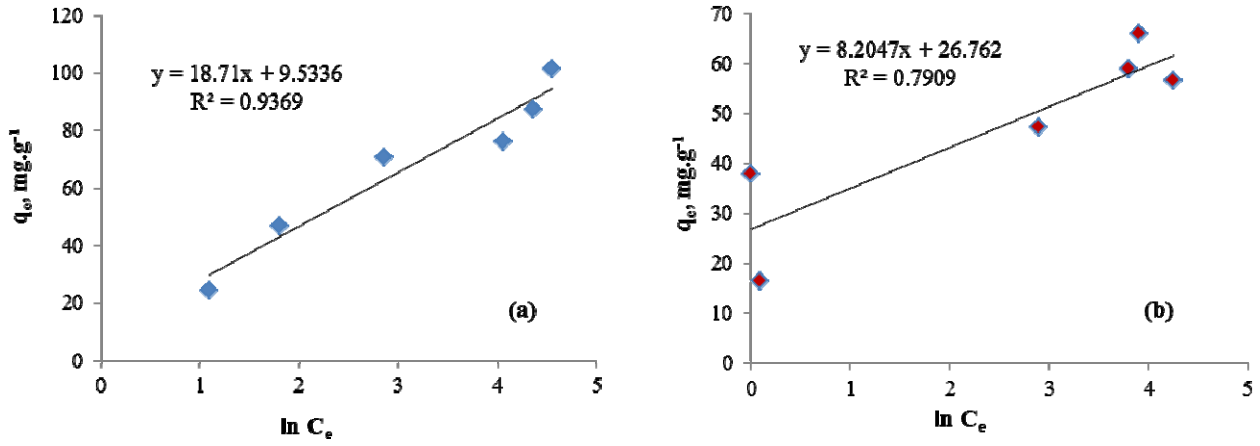

Figure 5. The plots of Temkin isotherm for adsorption of (a) Ag and (b) Zn ions over NH2 – MCM – 41. Amount of adsorbent 2 g L-1, pH = 7, initial concentration 200 mg L-1

Table 2. Langmuir, Freundlich and Temkin isotherms Data for Ag and Zn ions adsorption by NH2 – MCM – 41 nano porous adsorbent. Amount of adsorbent 2 g L-1, pH = 7, initial concentration 200 mg L-1

Metal ion	Langmuir				Freundlich			Temkin			
	q_m $mg.g^{-1}$	b $L.mg^{-1}$	R^2	R_L	K_F	n	R^2	q_e	b	A	R^2
Ag	111.11	0.095	0.977	0.033	1.33	3.00	0.889	28.24	5.30	3.53	0.936
Zn	62.50	0.470	0.983	0.007	24.94	4.90	0.973	85.27	9.21	2.46	0.940

Comparing the results from isotherm plots and experimental data, adsorption equilibrium of Ag and Zn ions is more convenient with Langmuir isotherm than Freundlich and Temkin isotherms. In the case of Ag ions Temkin isotherm somewhat may be convenient.

Desorption studies: Figure 6 shows desorption plots of Ag and Zn ions. Obtaining the value of desorption, 0.1M, 0.01M and 0.001M solutions of HCl were used. As it may be seen on figure 6, firstly desorption increase rapidly. These ions were adsorbed in pH = 7, therefore it is evident that desorption will occur in low pHs. Consequently, most suitable desorption occur in pH = 0 to 3. In this study, most suitable results were obtained at pH = 2. Thus, it seems that extraction and recovery of these ions is possible.

Conclusion

Experimental results show that the optimum condition for Ag and Zn ions over nano mesoporous NH2 – MCM – 41 adsorbent was obtained in pH = 7, amount of adsorbent = 2g.L^{-1} and initial concentration of metallic ions = 200 mg.L^{-1} [1]. Results of studies show that adsorption of these ions in optimum condition follows a pseudo-second order kinetics. The data obtained from pseudo-second order kinetics plots show acceptable consistence with experimental data. Considering the results obtained from isotherm studies, adsorption features may be interpret by Langmuir isotherm. These results suggest also, the possibility of extraction and recovery of these metallic ions from industrial wastes.

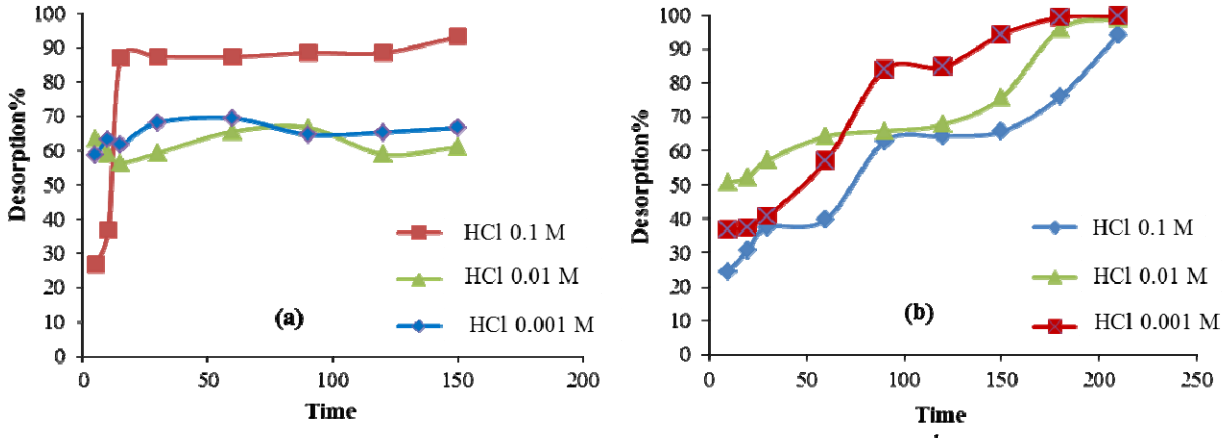

Figure 6. Desorption plots of (a) Ag and (b) Zn from NH2 – MCM – 41 adsorbent in pH = 2

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