# Adsorpative features of polyacrylamide- bentonite and zeolite composites for Cs<sup>+</sup> and Co<sup>2+</sup>

M. I. El- Dessouky<sup>1</sup>, E. H. El- Masry<sup>\*1</sup>, H. S. Hassan<sup>1</sup> and M. F. El- Shahat<sup>2</sup>

<sup>1</sup>Hot Labs, Atomic Energy Authority Inshas, Kaliobia, <sup>2</sup>Faculty of Science, Chemistry Dept., Ain Shams University, Cairo, Egypt \*emanelmasry74@yahoo.co.uk

**Abstract:** Polyacrlamide- Bentonite and polyacrylamide- Zeolite composites were synthesized and evaluated, as ion exchangers, for the removal of cesium and cobalt ions from aqueous solutions in batch operations. Batch experiments were carried out as a function of pH, initial ion concentration and temperature. Simple kinetic and thermodynamic models have been applied to the rate and isotherm sorption data and the relevant kinetic and thermodynamic parameters were determined from the graphical presentation of these models. [M. I. El- Dessouky, E. H. El- Masry, H. S. Hassan and M. F. El- Shahat, **Adsorpative features of polyacrylamide**-

[M. I. El-Dessouky, E. H. El-Masry, H. S. Hassan and M. F. El-Shahat. Adsorptive features of polyacrylamidebentonite and zeolite composites for  $Cs^+$  and  $Co^{2+}$ . Life Sci J 2012;9(1):1015-1024] (ISSN:1097-8135). http://www.lifesciencesite.com. 145

Key Words: Ion exchange/ Cesium and Cobalt ions / polyacrylamide/ Zeolite/ Bentonite.

# 1. Introduction

There are a number of liquid processes and waste streams at nuclear facilities that require treatment for process chemistry control reasons and/or the removal of radioactive contaminants. Cesium, cobalt and strontium are the most abundant radionuclides in nuclear fission products that are routinely or accidentally released. They have relatively long half-life of about 30 years and are considered as hazardous elements for the environment. Different techniques such as chemical precipitation, ion exchange, and evaporation are used for the treatment of aqueous waste solutions containing these ions. Ion exchange technique has become one of the most commonly used treatment methods for hazardous and radioactive aqueous streams due to its simplicity, selectivity and efficiency. A wide range of materials having different chemical and physical properties, which can be naturally occurring or synthetic, is available for this technique. Inorganic ion exchange materials have emerged as an increasingly important replacement or complement for conventional organic ion exchange resins, particularly in liquid radioactive waste treatment due to their radiation stability and greater selectivity for certain radiological important species, such as cesium, cobalt and strontium. In the last decade, the natural clay minerals, such as montmorillonite (MMT), kaolinite<sup>(1)</sup>, and palygorskite (attapulgite) <sup>(2)</sup>, are widely used in catalysis<sup>(3,4)</sup>, as adsorbents<sup>(5-14)</sup>, in nanocomposites<sup>(15-20)</sup>, in sensors<sup>(21)</sup>, electrode<sup>(22,24)</sup>, as antibacterial materials<sup>(25)</sup> and in nuclear waste treatment and storage<sup>(26-29)</sup>. Nowadays, surface modification of clay minerals has become increasingly important for improving the practical applications of clays and clay minerals<sup>(30)</sup>, Surface modification by polymers is found to be one of the

most effective methods, as the surface properties can be widely changed by a variety of functional polymers. The present work deals with the preparation and characterization of Polyacrlamide-Bentonite and Polyacrlamide- Zeolite composites and a series of experiments to assess the utility of these prepared composites for the removal of  $Cs^+$  and  $Co^{2+}$ ions from aqueous solutions under batch conditions. The relevant data, with respect to kinetic and equilibrium of the sorption and exchange of  $Cs^+$ and  $Co^{2+}$  ions, have been obtained using simple kinetic and thermodynamic models.

# 2. Experimental

# 2.1. Chemicals and reagents

All the reagents used in this work were of AR grade chemicals and were used without further purification. Cesium and Cobalt were supplied as cesium chloride and, Cobalt chloride, from Sigma–Aldrich Company. Stock solutions of the test reagents were prepared by dissolving CsCl and CoCl<sub>2</sub>.6H<sub>2</sub>O in distilled water.

# 2.2. Preparation

Includes the preparation of polyacrylamide, polyacrylamide- Bentonite and polyacrylamide-Zeolite composites. The preparation of polyacrylamide was carried out using Gamma radiation- initiated polymerization of acrylamide monomer in aqueous solution at a monomer concentration of 10% and a radiation does of 10 KGy/hr. the prepared polyacrylamide gel was used to prepare the Bentonite and Zeolite composites at the same radiation does.

# 2.3. Characterization

The crystallinity and functional groups of the

prepared material were investigated using X-Ray Diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR) and thermal analysis.

# 2.4. Batch sorption studies

Batch experiments were performed under kinetic and equilibrium conditions. To determine the pH range at which the maximum uptake of  $Cs^+$  and  $Co^{2+}$ ions would take place on the prepared composites. A series of 50 mL test tubes each containing 0.1 g of composite was filled with 10 mL of a desired concentration (10<sup>-4</sup>M). The initial pH was adjusted to values ranging from 2.0 to 8.0 using dilute solution of hydrochloric acid or Ammonia solution. The tubes were shacked for three hours to attain equilibrium. Preliminary investigations showed that the sorption process of each studied ion was completed after two hours. The suspension obtained was centrifuged to separate the solid from the liquid phase. The clear liquid phases obtained were used for the elemental analysis using Atomic Absorption Spectrophotometer (Buck scientific model VGP 210).

# 2.4.1. Kinetic studies

Kinetic studies were performed at three different temperatures (298, 313 and 333° K) for  $Cs^+$  and  $Co^{2+}$ ions at an initial ion concentration of 0 .01 M. For these investigations, 0.1 g of polyacrylamidebentonite and polyacrylamide- Zeoilte composite was contacted with 10 mL solution containing known concentration of  $Cs^+$  and  $Co^{2+}$  ions and the solution in the vial was kept stirred in a thermostat shaker adjusted at the desired temperature. A fixed volume (2 mL) of the aliquot was withdrawn as a function of time while the solution was being continuously stirred. Thus, the ratio of the volume of solution to the weight of the composite in the vial does not change from the original ratio. The withdrawn solution was centrifuged to separate the composite and a fixed volume (1 mL) of the clear solution was pipetted out for the determination of the amount of unsorbed metal ion still present in solution. The percent uptake was calculated using:

% uptake = 
$$\frac{\left(C_{\circ} - C_{t}\right)}{C_{\circ}} \times 100$$

Where  $C_o$  and  $C_t$  are the initial and equilibrium concentrations (mmol/L) of metal ion in solution.

(1)

# 2.4.2. Sorption equilibrium studies

In the experiments of sorption isotherm measurements, 10 mL of the metal ion solution of varying concentrations  $(10^{-4} \text{ to } 5 \times 10^{-2} \text{ M})$  were agitated with 0.1 g of the polyacrylamide- bentonite or Zeoilte composite at different temperatures (298,

## 313, and 333° K) and at initial

PH of 6.0. After the established contact time was reached, aliquots of supernatants were withdrawn and the amount of the metal ion retained in the composite phase (mg/g) was estimated. All batch experiments were carried out in duplicate and the mean values are presented. The metal concentration retained in the solid phase was calculated using the following equation:

 $q_e = \frac{(C_\circ - C_e)V}{M}$  (2) Where, Co and Ce are the initial and equilibrium

concentrations of metal ion in solution (mg/l),

V is the solution volume (l), and M is the weight of the solid (g)

M is the weight of the solid (g).

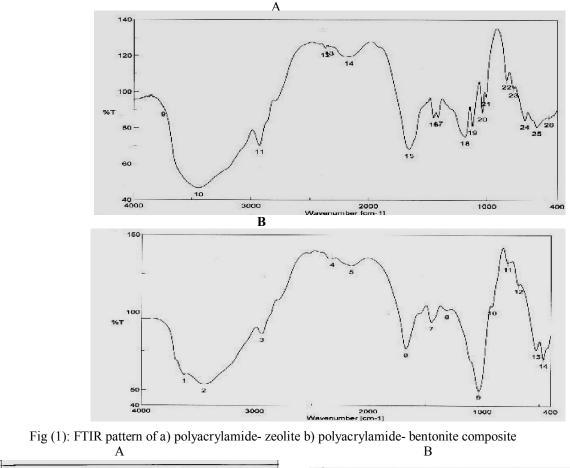
# 3. Results and Discussion

# **3.1.** Characterization of the prepared materials

The FT-IR spectra of the composites were compared in Fig (1).Broad and sharp appearance at 3200–3600 cm<sup>-1</sup> in the FT-IR spectra were of the bonded and free O-H stretches. The band at 1000-1700 cm<sup>-1</sup> and band at 400-700 cm<sup>-1</sup> corresponding to silicates. Bands at 1700, 3200cm<sup>-1</sup> are for C=O from amide group. Band at 2900 cm<sup>-1</sup> related to C-H group. Bands at 800 and 2500 cm<sup>-1</sup> are corresponding to Al-OH and Si-OH, respectively (31). It was found that, from the XRD pattern of polyacrylamidezeolite and polyacrylamidebentonite composites shown in fig (2), both of the composites are amorphous. Strong interaction between zeolite, bentonite and monomer in polymeric chains during synthesis takes place and leads to absence of diffraction peaks <sup>(32)</sup>. TGA and DTA curves show that the composites are thermal stable at temperature greater than 300°C.

## 3.2. Effect of pH

The effect of pH on the sorption removal of  $Cs^+$  and  $Co^{2+}$  ions from aqueous chloride solutions using prepared polyacrylamide- bentonite and polyacrylamide- Zeoilte composite material was investigated over the pH range from 2.0 to 8.0. It was observed that each metal ion sorption process is dependent on the initial pH of the solution and the amount of metal ion sorbed increased with increase in the pH value. At lower values, the metal ion uptake was inhibited in this acidic medium and this can be attributed to the presence of H<sup>+</sup> ions competing with the  $Cs^+$  and  $Co^{2+}$  ions f or the sorption sites. The uptake continuously increases with the increase in pH value and the highest uptake was observed at pH range from 6.0 to 8.0. Also the increasing of the pH value decreases the degree of protonation of the amid and amino groups cross linking between polymeric chains which leads to in an increase in the probability of interaction between composites and metal ions<sup>(32)</sup>.



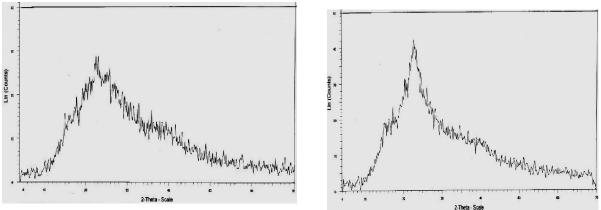


Fig (2): XRD pattern of a) polyacrylamide- zeolite b) polyacrylamide- bentonite composite

### 3.3. Effect of contact time

The variation of the amounts of  $Cs^+$  and  $Co^{2+}$ ions sorbed at different time intervals, for the fixed initial ion concentration of 0.01 M and at different sorption temperatures of 298, 313 and 333° K are represented in Figs (3, 4). From these figures it can be concluded that the amount of the sorbed  $Cs^+$  and  $Co^{2+}$  ions increases with the increase in temperature indicating an endothermic nature of the sorption processes, while the time required reaching equilibrium remained practically unaffected . **3.4. Sorption kinetic** 

To describe the changes in the sorption of metal ions with time, three simple kinetic models were tested. The rate constant of each metal ion removal from the solution by polyacrylamide- bentonite and polyacrylamide- Zeoilte composite was determined using pseudo first-order and pseudo second-order rate models.

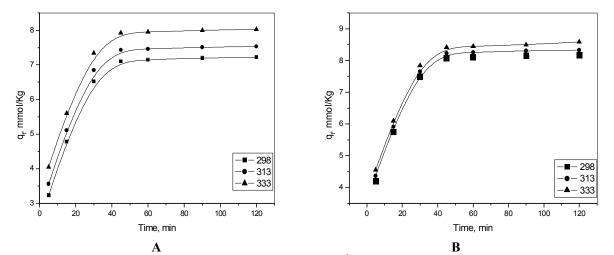


Fig. (3): Effect of contact time on sorption of a) Cs<sup>+</sup> and b) Co<sup>2+</sup> ions onto PAM- Zeolite composite at different temperatures.

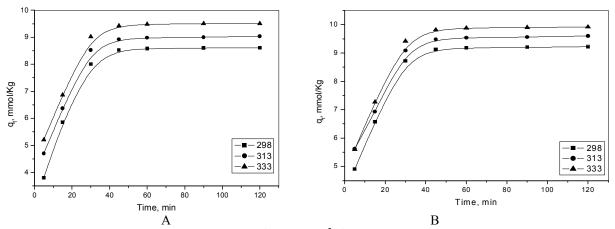


Fig (4): Effect of contact time on sorption of (a)  $Cs^+$  and (b)  $Co^{2++}$  ions onto PAM- Bentonite composite

### The pseudo first order model

The sorption kinetics of metal ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple pseudo first-order model <sup>(33)</sup> was therefore used to correlate the rate of reaction and expressed as follows:

$$Log (q_e-q_t) = log q_e - \frac{R_2}{2.303}t$$
 (3)

where  $q_e$  and  $q_t$  are the concentrations of ion in the adsorbent at equilibrium and at time t, respectively (mmol/g) and  $k_1$  is the pseudo first-order rate constant (min<sup>-1</sup>). The sorption of metal ions was tested using the pseudo first order model, although the linear correlation coefficients of the plots are so good, the qe (calculated) values are not in agreement with qe (experimental) for all studied sorption processes. So, it could suggest that the sorption of Cs<sup>+</sup> and Co<sup>2+</sup> metal ions onto polyacrylamide- Zeolite and polyacrylamide- bentonite composites is not a first-order reaction. (Figures were omitted because the model is not applicable).

#### The pseudo second order model

A pseudo second-order rate model <sup>(34)</sup> is also used to describe the kinetics of the sorption of ions onto adsorbent materials.

$$\frac{t}{q} = \frac{1}{K_2 q_{\theta}^2} + \frac{1}{q_{\theta}} t \tag{4}$$

Where  $k_2$  is the rate constant of pseudo second-order equation. The qe and  $K_2$  values of the pseudo second-order kinetic model can be determined from the slope and the intercept of the plots of t/q versus t, respectively. The compatibility of experimental data to the second-order kinetics model was evaluated. The kinetic plots of t/qt versus t for both Cs<sup>+</sup> and Co<sup>2+</sup> ions sorption at different temperatures are presented in Figs. (5, 6). The relation is linear, and the correlation coefficient (R<sup>2</sup>), suggests a strong correlation between the parameters and also explains that the sorption process of each ion follows pseudo second-order kinetics. The product  $k_2q_{e2}$  is the initial sorption rate represented as  $h = k_2q_{e2}$ . From Table (1), it can be shown that the values of the initial sorption rate (h) and rate constant (K<sub>2</sub>) were increased with the increase in temperature. The correlation coefficient R<sup>2</sup> has an extremely high value

(>0.99), and its calculated equilibrium sorption capacity ( $q_e$ ) is consistent with the experimental data. These results explain that the pseudo second order sorption mechanism is predominant and that the overall rate constant of each sorption process appears to be controlled by the chemical sorption process <sup>(35)</sup>.

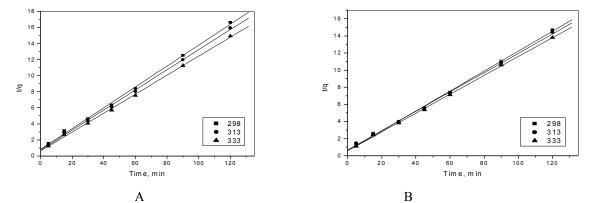


Fig.(5): Peseudo second order plots for a)  $Cs^+$  and b)  $Co^{2+}$  ions onto PAM- Zeolite composite at different temperatures.

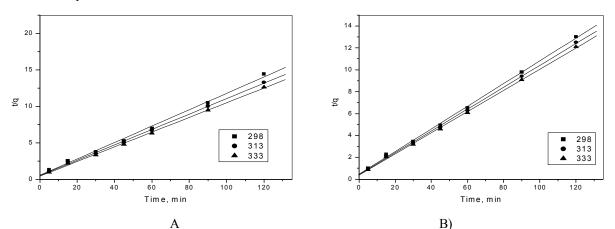


Fig.(6): Peseudo second order plots for a) Cs<sup>+</sup> and b) Co<sup>2+</sup> ions onto PAM- Bentonite composite at different temperatures.

Table (1): The calculated parameters of the pseudo second-order kinetic model for  $Cs^+$  and  $Co^{2+}$  ions sorbed onto PAM- Bentonite and PAM- Zeolite composites at different sorption temperatures

	Temp., K		olite	PAM- Bentonite					
Metal ion		K <sub>2</sub> , g/mmol.min	<i>q<sub>e,</sub></i> calc. mmol∕kg	<i>qe exp</i> mmol/kg.	$R^2$	K2, g/mmol. min	<i>q<sub>e,</sub></i> calc. mmol/kg	<i>qe exp</i> mmol/kg.	$R^2$
	298	0.02	8.9	8.6	0.996	0.021	7.7	7.2	0.996
Cs <sup>+</sup>	313	0.02	9.5	9.0	0.998	0.022	8.0	7.51	0.998
	333	0.03	9.9	9.5	0.998	0.023	8.3	8.0	0.998
	298	0.022	10.0	9.2	0.998	0.025	8.3	8.15	0.998
Co <sup>++</sup>	313	0.023	10.1	9.56	0.998	0.02	9.1	8.31	0.997
	333	0.025	10.3	9.9	0.998	0.02	10.0	8.50	0.999

### 3.5. Sorption isotherms

Sorption equilibrium is usually described by an isotherm equation whose parameters express the

surface properties and affinity of the sorbent, at a fixed temperature and pH. An adsorption isotherm describes the relationship between the amount of

adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. In this concern, the sorption isotherms for removal of Cs<sup>+</sup> and Co<sup>2+</sup> ions from aqueous solutions onto polymer composites at three different temperatures were determined as shown in Figures (7, 8). The isotherms are regular, positive. The convex isotherms at high concentrations indicated that sorption was reduced <sup>(36)</sup>. The initial rapid sorption gives way to a slow approach to equilibrium at higher ion concentrations. These results reflect the efficiency of polymer for the removal of Cs<sup>+</sup> and Co<sup>2+</sup> ions from aqueous solution in a wide range of concentrations. The uptake of ions increased with the increase in temperature thereby indicating the process to be endothermic.

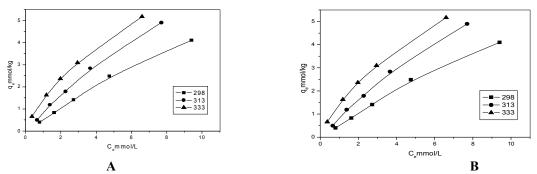
### 3.6. Isotherm models Freundlich Isotherm model

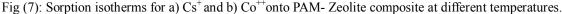
Freundlich equation is derived to model the multilayer sorption and for the sorption onto heterogeneous surfaces. The logarithmic form of Freundlich equation may be written as:

 $\log q_e = \log K_f + (1/n) \log C_{e} \quad (5)$ 

where,  $q_e$  is the amount of metal ion sorbed per unit weight of sorbent (mmol/kg),  $C_e$  is the equilibrium concentration of the metal ion in the equilibrium solution (mmol/L), K is constant indicative of the

relative sorption capacity (mmol/kg) and 1/n is the constant indicative of the intensity of the sorption process. The pictorial illustration of log q<sub>e</sub> vs. log C<sub>e</sub> is shown in Figs. (9,10) which suggests that the sorption of  $Cs^+$  and  $Co^{2+}$  ions obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants 1/n and K<sub>f</sub> are computed from the slope and the intercepts, by means of a linear least square fitting method, and also given in Table (2). It can be seen from these data that the Freundlich intensity constant (n) are greater than unity for all studied ions. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between metal ions species and the composite. In our case, n > 1 for all ion species, the composite shows an increase tendency for sorption with increasing solid phase concentration. This should be attributed to the fact that with progressive surface coverage of adsorbent, the attractive forces between the metal ion species such as van der Waals forces, increases more rapidly than the repulsive forces, exemplified by short-range electronic or long-range Coulombic dipole repulsion, and consequently, the metal ions manifest a stronger tendency to bind to the active sites of the compo site (37)





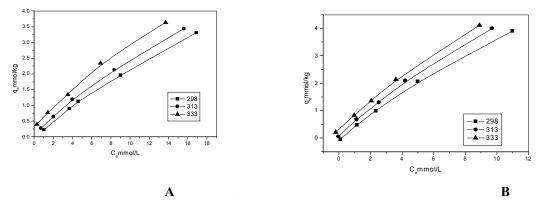


Fig (8): Sorption isotherms for a) Cs<sup>+</sup> and b) Co<sup>++</sup> onto PAM- Bentonite composite at different temperatures.

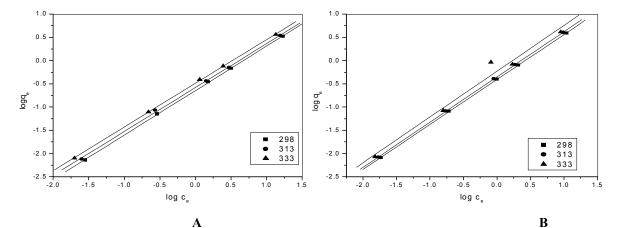


Fig.(9): Freundlich isotherm plots for the sorption of (a) Cs<sup>+</sup>and (b) Co<sup>2+</sup> ions onto PAM- Zeolite composite at different temperatures

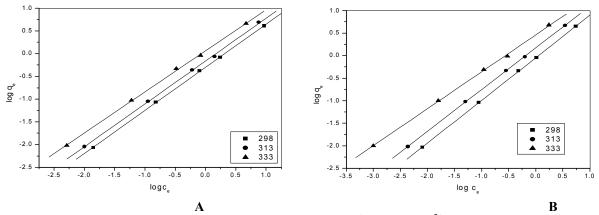


Fig. (10): Freundlich isotherm plots for the sorption of (a) Cs<sup>+</sup> and (b) Co<sup>2+</sup> ions onto PAM- Bentonite composite at different temperatures

### Langmuir Isotherm model

Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by the following formula:

$$(C_e / q_e) = (1/Q^{\circ}b) + (1/Q^{\circ})C_e$$
<sup>(6)</sup>

Where,  $q_e$  is the amount of metal ion sorbed per unit weight of adsorbent (mmol/g),  $C_e$  is the equilibrium concentration of the metal ion in the equilibrium solution (mmol/L),  $Q_o$  is the monolayer adsorption capacity (mmol/g) and b is the constant related to the free energy of adsorption (b  $\alpha e^{-\Delta G/RT}$ ). Applying Langmiur isotherm by plotting  $C_e/q_e$  vs.  $C_e$  as shown in Figs (11, 12) for Cs and Co respectively straight lines are obtained for the three ions, confirming that this expression is indeed a reasonable representation of chemisorption isotherm. The Langmuir constants  $Q_o$  and b for sorption of ions onto polymer, as showed in table (3), increased with temperature showing that the sorption capacity and intensity of sorption are enhanced at higher temperatures. This increase in sorption capacity with temperature suggested that the active surfaces available for sorption have increased with temperature. One of the essential characteristics of the Langmuir model could be expressed by dimensionless constant called equilibrium parameters  $R_L^{(38)}$ 

$$R_L = 1/(1+b C_o)$$
 (7)

where,  $C_o$  is the highest initial metal ion concentration (mmol/L). The value of  $R_L$  indicates the type of isotherm to be irreversible ( $R_L=0$ ), favorable ( $0<R_L<1$ ), linear ( $R_L=1$ ), or unfavorable ( $R_L>1$ ). All the  $R_L$  values were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of all metal ions. High values of regression coefficients between the sorbate and sorbent systems for both Langmuir and Freundlich models (around 0.99) indicated the applicability of this resin system for  $Cs^+$  and  $Co^{2+}$ removal in both monolayer sorption and heterogeneous surface conditions.

Metal		PAM- Bentonite			PAM- Zeolite			
ion	Temp.,k	1/n	K,mmol/kg	$\mathbf{R}^2$	1/n	K,mmol/kg	$\mathbf{R}^2$	
	298	0.90	1.15	0.998	0.94	3.1	0.992	
Cs	313	0.94	1.58	0.998	0.95	3.8	0.992	
	333	0.95	2.00	0.997	0.96	4.4	0.995	
	298	0.82	1.12	0.991	0.97	1.66	0.996	
C	313	0.93	1.50	0.993	0.97	2.24	0.999	
Со	333	0.95	2.57	0.998	0.98	2.9	0.998	

Table (2): Freundlich parameters for sorption of Cs<sup>+</sup> and Co<sup>2+</sup> onto PAM- Bentonite and PAM- Zeolite composites

Table (3): Langmuir parameters for sorption of Cs<sup>+</sup>and Co<sup>2+</sup> ions onto PAM- Bentonite and PAM- Zeolite composites.

Metal	Temp.,k	PAM- Bentonite				PAM- Zeolite				
ion		Q <sub>0</sub> , mmol/kg	b, l/mmol	$\mathbf{R}^2$	R <sub>L</sub>	Q <sub>0</sub> , mmol/kg	b, l/mmol	$\mathbf{R}^2$	R <sub>L</sub>	
	298	23.7	0.25	0.988	0.074	56.8	0.08	0.981	0.20	
Cs	313	27.1	0.44	0.988	0.043	76.9	0.16	0.982	0.11	
-	333	33.5	1.70	0.999	0.012	135.1	0.20	0.991	0.09	
	298	44.8	0.50	0.991	0.040	104.2	0.09	0.979	0.18	
Со	313	49.0	1.20	0.997	0.020	155.0	0.11	0.999	0.15	

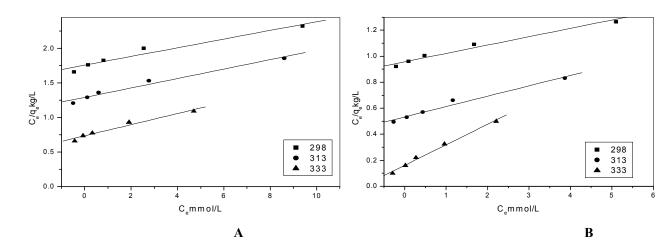


Fig (11): Langmiur isotherms for a) Cs<sup>+</sup> and b) Co<sup>+</sup> <sup>+</sup>onto PAM- Zeolite composite at different temperatures.

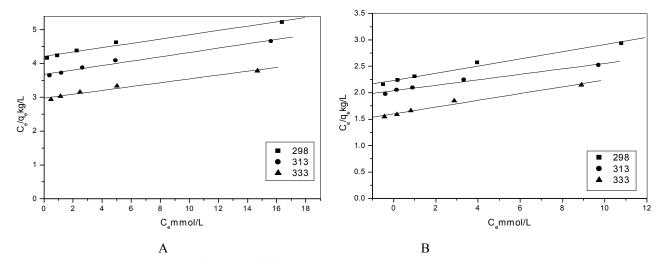


Fig (12): Langmiur isotherms for a) Cs<sup>+</sup> and b) Co<sup>+ +</sup>onto PAM- Bentonite composite at different temperatures.

### 3.7. Thermodynamic studies

To calculate the different thermodynamic parameters, Vant Hoff equation was used which is given as follow <sup>(39)</sup>.

 $\Delta G$ = -2.303RT logK<sub>c</sub> therefore, logK<sub>c</sub>= -  $\Delta G/2.303$ R (1/T) Therefore,

$$\log K_{c} = \frac{\Delta F}{2.303R} - \frac{\Delta H}{2.503R} \frac{1}{7}$$
(8)

 $\Delta G$ : is the free energy, T: is the absolute temperature in Kelvin, R: is the general gas constant (R=8.314 J/mol. K),  $\Delta H$ : is the enthalpy change,  $\Delta S$ : is the entropy change and K<sub>c</sub> is the equilibrium

entropy change ( $\Delta$ S) calculated from the slope and intercept of the plot of log K<sub>c</sub> versus 1/T, shown in Fig (15), are also given in Tables (5, 6).The change in  $\Delta$ H for all ions were found to be positive confirming the endothermic nature of the sorption processes.  $\Delta$ S values were found to be positive due to the exchange of the metal ions with more mobile ions present on polyacrylamide- Zeolite and polyacrylamide-Bentonite composites towards Cs<sup>+</sup>, Co<sup>2+</sup> and Sr<sup>2+</sup> ions, which would cause increase in the entropy during the sorption process.

constant. The values of enthalpy change ( $\Delta H$ ) and

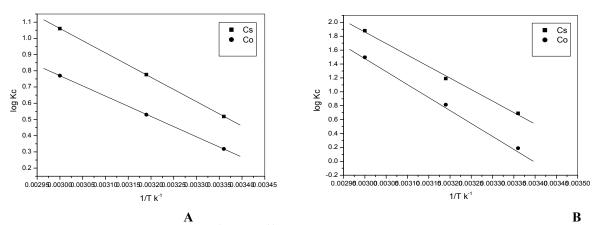


Fig (13): Vant Hoff plots for sorption of Cs<sup>+</sup> and Co<sup>++</sup> ions onto a) PAM- Zeolite, b) PAM- Bentonite at three different temperatures

Table (5): Values of the thermodynamic parameters for the sorption of  $Cs^+$  and  $Co^{2+}$  ions onto PAM- Zeolite composite.

Tama la	kc		∆G,kj/mol		ΔH, kj/mol		∆S, kj/mol	
Temp,k	Cs <sup>+</sup>	Co <sup>2+</sup>						
298	2.71	1.50	-2.45	-1.03		24.0	69.0	86.2
313	5.67	1.90	-4.49	-1.68	20.0			
333	11.43	2.20	-6.76	-2.17	_			

Table (6): Values of the thermodynamic parameters for the sorption of Cs<sup>+</sup> and Co<sup>2+</sup> ions onto PAM- Bentonite site

Tama la	kc		∆G,kj/mol		ΔH, kj/mol		ΔS, kj/mol	
Temp, k	Cs <sup>+</sup>	Co <sup>2+</sup>						
298	4.90	1.17	-3.94	-0.40				
313	15.60	7.70	-7.13	-5.33	63.40	71.40	226	243
333	75.00	26.15	-12.00	-9.05				

### 4. Conclusion

In this study, the preparation and characterization of PAM–Zeolite and Bentonite composites and its comparative adsorptive features with bare Zeolite and Bentonite were investigated for  $Cs^+$  and  $Co^{2+}$  removal. The FTIR and XRD analysis showed that PAM–Zeolite and Bentonite composites had a hybrid composition of PAM and Zeolite or Bentonite resembling colloidal dispersion of one solid phase in another. Sorption experiments were performed for the removal of cesium, cobalt and strontium ions from their aqueous solutions using the two composites. The kinetic modelings suggest that, the pseudo second-order mechanism is predominant and that the overall rate constant of ions appears to be controlled by the chemisorption mechanism. Experimentally obtained isotherms were well compatible to Langmuir and Freundlich models, from which the derived parameters were, confirmed each other. Measurements of  $\Delta G_o$  are a negative value confirmed the adsorption reactions occurred spontaneously at a given temperature.

#### **Corresponding author**

E. H. El- Masry

Hot Labs, Atomic Energy Authority Inshas, Kaliobia, emanelmasry74@yahoo.co.uk

#### References

- Murray H.H. (2000) Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. Applied Clay Science. 17:207–221.
- Galan E. (1996) properties and applications of palygorskite-sepiolite clays Clay Minerals, 31:443–453.
- 3. De Stefanis A. (2006). A.A.G. Tomlinson towards designing pillared clays for catalysis. Catal. Today, 114:126–141.
- Gournis D., M.A. Karakassides, T. Bakes, N. Boukos, D. Petridis (2002) Catalytic synthesis of carbon nanotubes on clay minerals, Carbon 40, 2641–2646.
- Tank S.Y., R.W. (1985) Determination of Chromium Speciation in Environmental Particles, Technique study of Ferrochrome Smelter dust. A review. Appl. Clay Sci., 1: 145–162.
- Smith E.H., T. Vengris(1998) "Clay Minerals and Heavy Metals.", Crit. Rev. Anal. Chem. 28:13–18.
- Huh J.K., D.I Song., Y.W. Jeon, (2000) Sequential competitive sorption and desorption of chlorophenols in organoclay. Sep. Purif. Technol., 35:243–259.
- Cox M., J.R. Rus-Romero, T.S. Sheriff (2001) The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution - Part I. The preparation of clays impregnated with di-(2-ethylhexyl) phosphoric acid and their use for the removal of copper(II). Chemical Engineering. J., 84:107–113.
- Pal O.R., A.K. Vanjara (2001) Removal of malathion and butachlor from aqueous solution by clays and organoclays.. Sep. Purif. Technol., 24:167–172.
- Adebajo M.O., R.L. Frost, J.T. Kloprogge, O. Carmody, S. Kokot (2003) Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. J. Porous Material 10, 159–170.
- Li, H., Teppen, B.J., Laird, D.A., Johnston, C.T., Boyd, S.A. (2004) Thermodynamics of Nitroaromatic Compound Adsorption from Water by Smectite Clay Environ. Sci. Technol., 38:5393–5399.
- Lin J.J., Y.M. Chen(2004) Amphiphilic Properties of Poly(oxyalkylene)amine Intercalated Smectite Aluminosilicates. Langmuir, 20:4261–4264.
- Jaber M., J. Miehe-Brendle, L. Michelin, L. Delmotte(2005) Heavy Metal Retention by Organoclays Synthesis, Applications, and Retention Mechanism.. Chem. Mater., 17:5275–5281.
- Dias Filho N.L., D.R. Do Carmo (2006) Study of an organically modified clay: Selective adsorption of heavy metal ions and voltammetric determination of mercury(II). Talanta, 68: 919–927.
- Giannelis E.P. (1996) Polymer Layered Silicate Nanocomposites review. J. Advanced Materials, 8:29–35.
- J.W. Gilman, Flammability and Thermal Stability Studies of Polymer Layered-Silicate Clay Nanocomposites. Applied Clay Science 15, (1999) 31–49.
- P.C. LeBaron, Z. Wang, T.J. 'Polymer-layered silicate nanocomposites: an overview, 'Pinnavaia,. Applied Clay Science 15, (1999) 11–29.
- A.B. Morgan, P. Dubois, "Polymer-Layered Siliate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials ",Material Science and Engineering 28, (2000) 1–63.
- 19. S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposite: a review from preparation to processing. Progress in Polymer

Science 28, (2003) 1539-1641.

- S.J. Ahmadi, Y.D. Huang, W. Li, J. Synthetic routs, properties and future application of polymer-layered silicate nanocomposites Material Science. 39, (2004) 1919–1925.
- M. Darder, M. Colilla, E. Ruiz-Hitzky," Chitosan -clay nanocomposites: application as electrochemical sensors", Applied Clay Science 28, (2005) 199–208.
- U. Guth, S. Brosda, Applications of clay minerals in sensor techniques J. Schomburg, Applied Clay Science 11, (1996) 229–23 6.
- J.M. Zen, Analytical Chemistry 76, (2004) The Prospects of Clay Mineral Electrodes205A–211A.
- 24. I.K. Tonle, E. Ngameni, A. Walcarius, Sens. Actuators, B, Chem. 110, (2005) Preconcentration and voltammetric analysis of mercury (II) at a carbon paste electrode modified with natural smectite-type clays grafted with organic chelating groups195–203.
- L.B. Williams, M. Holland, D.D. Eberl, T. Brunet, L.B. De Courrsou, Mineral. Soc. Bull. 139, (2004) Killer clays! Natural antibacterial clay minerals.3–8.
- A. Meunier, B. Velde, L. Griffault, Reactivity of bentonites: a review. Clay Miner. 33, (1998) The reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage 187–196.
- A.M. El-Kamash, M.R. El-Naggar, M.I. El-Dessouky, Proceedings of the first scientific environmental Conference, ZAGAZIG UNIV. (2006) Two-step method for preparation of NaA-X zeolite blend from fly ash for removal of cesium ions 221-231.
- 28. A.M. El-Kamash, Journal of Hazardous Materials, (2007) Evaluation of zeolite A for the sorptive removal of Cs< sup>+</sup> and Sr< sup> 2+</sup> ions from aqueous solutions using batch and fixed bed column operations.
- 29. A.M. El-Kamash, N.M. Sami, M.I. El-Dessouky, International journal of Physical Scinces, 2(1) (2007) LEACHI\_G BEHAVIOUR OF 137Cs A\_D 60Co RADIOUCLIDES FROM STABILIZED WASTE MATRICES, 1.
- C.J. van Oss, R.F. Giese, J. Dispers. Sci. Technol. 24, (2003) Surface Modification of Clays and Related Materials363–376.
- U. Ulusoy and S. Simsek; J. Hazardous materials, 127, 1-3(2005) Lead removal by polyacrylamide-bentonite and zeolite composites: Effect of phytic acid immobilization 163.
- 32. A. A. El- zahhar, H. M. abdel- aziz and T. Siyam; 8th Arab international conference on polymer science and technology, (2005) Some synthesized polymeric composite resins for the removal of Co(II) and Eu(III) from aqueous solutions.
- Y.S. Ho, G. McKay, Resour. Conserv. Recycling 25 (1999) A kinetic study of dye sorption by biosorbent waste product pith 171-193.
- 34. G. McKay, Y. S. Ho, Process Biochem. 34 (1999) Pseudo-second order model for sorption processes 451 460.
- G. McKay, Y. S. Ho, Water Res. 33 (1999) The sorption of lead(II) ions on peat 587-585.
- J. Peric, M. trgo, N. V. Medvidovic, Water Res. 38 (2004) Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms 1839-1899.
- 37. K.M Abd El-Rahman, A.M. El-Kamash, M.R. El-Sourougy, N.M. Abdel- Moniem J. Radioanl. Nucl. Chem. 268 (2006) Thermodynamic modeling for the removal of Cs+, Sr 2+, Ca 2+ and Mg 2+ ions from aqueous waste solutions using zeolite A 221-230.
- D. Mohan, S. C. J. Colloid Interface Sci. 299 (2006) Intrinsic paramagnetic defects probe superionic phase transition in Ag1-xCuxI (x=0, 0.05, 0.15 and 0.50) nanocrystals 76-57.
- M. I. Panayotova, Waste Manag., 21 (2001) Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite671-676.

1/6/2012