Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Ni(II) and Co(II) Using Microballoons Containing Mg-Silicate and CYANEX923 Prepared by the Emulsion Liquid Membrane System

M. S. Gasser[a]
[a] Hot Labs Centre, Atomic Energy Authority, Cairo, Egypt

To cite this Article Gasser, M. S.(2009) 'Adsorption of Ni(II) and Co(II) Using Microballoons Containing Mg-Silicate and CYANEX923 Prepared by the Emulsion Liquid Membrane System', Separation Science and Technology, 44: 4, 937 — 953
To link to this Article: DOI: 10.1080/01496390802437248
URL: http://dx.doi.org/10.1080/01496390802437248

Separation Science and Technology, 44: 937–953, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802437248

Taylor & Francis
Taylor & Francis Group

Adsorption of Ni(II) and Co(II) Using Microballoons Containing Mg-Silicate and CYANEX923 Prepared by the Emulsion Liquid Membrane System

M. S. Gasser
Hot Labs Centre, Atomic Energy Authority, Cairo, Egypt

Abstract: The Mg-silicate microballoons containing CYANEX923 were prepared by W/O/W emulsion. The diameter of obtained micro-sphere particles was ~10 μm and shell thickness was 2 μm. The adsorption of Co(II) and Ni(II) from aqueous solutions using prepared micro-sphere particles was investigated. Experiments were carried out as a function of solute concentration and temperature (25–60°C). Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the adsorption process. Equilibrium adsorption data were analyzed using Langmuir isotherm model. The results indicated that prepared micro-sphere particles can be used as an efficient adsorbent for the removal of Ni(II) and Co(II) from aqueous solution.

Keywords: CYANEX923, Co(II), emulsion, microballoon, Ni(II)

INTRODUCTION

The fact that cobalt and nickel usually appear together in ores, the similar physical and chemical properties of these metals and the high purity degree required in their applications have led to the development of a remarkable amount of research work on cobalt and nickel recovery

Received 29 February 2008; accepted 15 July 2008.

Address correspondence to M. S. Gasser, Hot Labs Centre, Atomic Energy Authority, Cairo 13759, Egypt. E-mail: mona_gasser@yahoo.com

and separation. Most of these studies concerned solvent extraction processes using organophosphorus acid extractants such as di(2-ethylhexyl)-phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis(2,4,4-trimethylpentyl) phosphinic acid (CYANEX272). CYANEX923 has gained prominence as extractant during the last decade because of its marked selectivity, hydrolytic stability, and easy phase separations (1,2). Extractive spectrophotometric determination of Co(II) in synthetic and pharmaceutical samples using CYANEX923 was studied and the results of the proposed method are comparable with atomic absorption spectrometry and were found to be in a good agreement. Cobalt has many industrial applications, where it is used to produce some alloys with iron, nickel, chromium and manganese (3). The recovery of cobalt from spent catalysts using CYANEX923 has been studied (4). As Co(II) was quantitatively extracted, the commercial utility of the extractant is demonstrated by recovery of high purity of Co(II) from spent catalysts.

Although liquid-liquid extraction is presently one of the major techniques for the separation and recovery of metal ions in many industrial fields, it has not been used in a limited commercial process because of certain disadvantages. One of these is the loss of the organic in the aqueous phase due to its solubility in the feed. A method to overcome this disadvantage involves immobilizing the extractant through microencapsulation. Compared to conventional liquid–liquid extraction, there are several advantages with solvent microcapsule as separation agent, including large specific interfacial area, high selectivity, minimal use of organic solvents, and ease of phase separation. Microencapsulation can therefore address the problems of phase separation, phase mixing, leakage of extractant as well as eliminate the need for complicated equipment in the extraction process. Recently, microcapsules prepared by various techniques have been widely studied for their potential applications in the pharmaceutical, agricultural, and chemical industries and especially for their utility in the separation and recovery of metal ions (5–11). Inorganic micro-sphere particles are applicable to microcapsules with an inorganic wall material, which are more advantageous than those with a polymeric wall material, regarding chemical durability, wear resistance, thermal resistance, etc. Several techniques for preparing inorganic micro-sphere particles have been reported (12–16).

In this paper, CYANEX923 immobilized in Mg-micro-sphere particles were prepared and characterized. Further, the adsorption of Ni(II) and Co(II) by the micro-sphere particles was investigated in terms of the adsorption kinetics and other parameters involved.

EXPERIMENTAL

Materials

Metal chlorides used were supplied by Fluka. Sodium silicate, cyclohexan, and Span 80, were AR grade and obtained from Merck Company (Germany). CYANEX923 kindly supplied by Cytec Inc., USA was used as received.

Preparation of Mg-Silicate Micro-Sphere Particles and Characterization

Mg-silicate micro-balloons were prepared by an inter-facial reaction method, which is based on an ion exchange reaction between the internal and external aqueous phases through the participation of a cation transport carrier added in the oil phase. Aqueous sodium silicate solution (Na_2SiO_3) (25 ml) of 1 M concentration and cyclohexane solution (25 ml) dissolving Span 80 as a surfactant 1% v/v and 0.25 M CYANEX923 as a cation carrier were used as aqueous and organic solutions, respectively. These solutions were mixed with a homogenizer (ultra high speed motor as well as a specially designed turbine plexi glass impeller, Cold, stream Eng. Ltd., UK.) at fixed stirring speed (5000 rpm, 5 min) to prepare W/O emulsion. Then, the emulsion was poured into 1 M aqueous Mg-chloride solutions (100 ml). The multiple emulsions (W/O/W emulsion) were stirred at 400 rpm for 60 min. The solid product obtained was filtered off, washed, and dried. The experiments were performed at room temperature.

The morphology of the micro-sphere particles was determined by a scanning electron microscope (SEM: JSM-6060, JOEL). The concentrations of sodium and Mg(II) in an external aqueous solution were measured by atomic absorption spectrometer (Buck scientific model VGP 210).

Kinetic Measurements

Kinetic studies were investigated in beakers 25 ml by taking 0.1 g of prepared Mg-micro-sphere particles containing CYANEX923 in 10 ml of aqueous solution containing known concentration of metal ion (0.08 M for each metal ion) at pH = 5.5 and 25°C. The solution in the beakers was kept stirred in a thermostat shaker adjusted at the desired temperature. One beaker was withdrawn as a function of time while the solution in the other beakers was being continuously stirred. Thus, the ratio of the volume of solution to the weight of adsorbent in the beaker does not change from the original ratio. The solution in the withdrawn beaker was filtrated to separate the adsorbent and a fixed volume (2 ml) of the solution was pipetted out for the determination of the amount of unabsorbed metal ion still present in solution. The concentration of Ni(II) and Co(II) in the aqueous solution was spectrophotometrically (17) determined by measuring its maximum absorbance at 393 and 515 nm, respectively, using a Shimadzu double beam recording spectrophotometer model 160 A. The temperature was adjusted over the range 25–60°C.

Adsorption Isotherms

Batch adsorption studies of Ni(II) and Co(II) were performed to obtain the equilibrium isotherms. For isotherm studies, a series of 25 ml test tubes were employed. Each test tube was filled with 10 ml of each metal ion solution of varying concentrations (0.08–1 M) and a known amount of adsorbent (micro-sphere particles) (0.5 g) was added into each test tube and agitated for a sufficiently long time ($\sim$3 h) required to reach equilibrium. The amount of metal ion retained in the adsorbent phase, q_e (mmol/g), was calculated using:

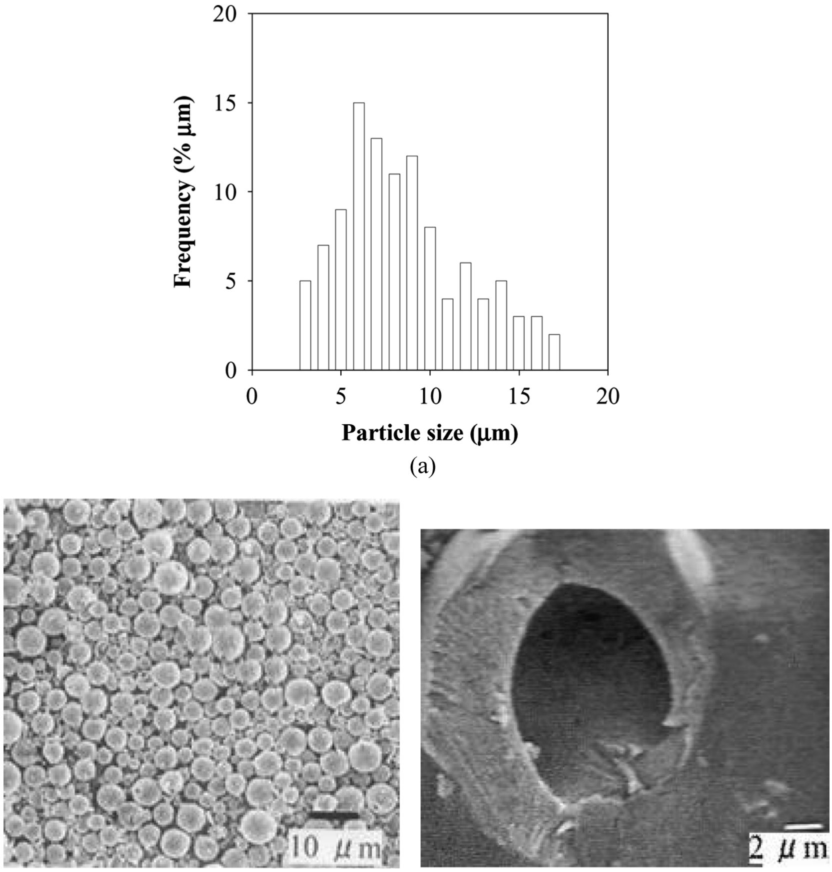
$$q_e = (C_0 - C_e)V/m \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mmol/l) of metal ion in solution, V is the volume (l) and m the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

Micro-Sphere Particles Characterization

The particle size distribution and SEM photograph of prepared Mg-silicate micro-sphere particles with internal and external aqueous solutions concentration of 1 M is shown in Figs. 1a, b; micro-sphere particles were formed under a secondary emulsification. As a result, most of the Mg-micro-sphere particles existed in the range of 6–10 μm diameter. From these photographs, it is evident that microparticle prepared by an interfacial reaction method was nearly spherical in shape and have smooth surface. Fig. 1c showed the SEM photographs of the cross-section of Mg-silicate micro-sphere particles obtained with internal and external aqueous solution concentration of 1 M. From these photographs, it is



(a)

(b)

(c)

Figure 1. Particle size distribution and SEM photograph of Mg-micro-sphere particles. (a), (b) photograph of the surfeace (c) photograph of cross-section.

evident that micro-sphere particles prepared by an interfacial reaction method are nearly spherical in shape and have a smooth surface.

Figure 2 shows the effect of internal and external aqueous solution concentrations on particle diameter. With the increase of concentration of internal and external aqueous solutions, the particle diameter of the micro-sphere particles increased clearly. The increase of the particle diameter was brought about by the increase of the water drops diameter in W/O emulsion, which is a commonly observed effect in the formation of emulsion (18). In order to prepare the micro-sphere particles with a large diameter, the internal and external aqueous solution concentrations were

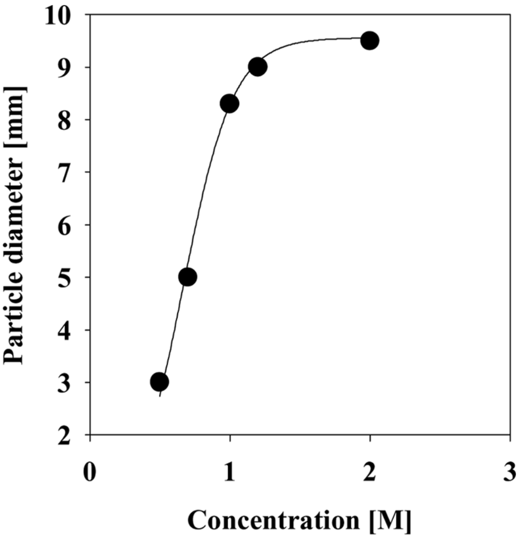


Figure 2. Effect of concentration of internal and external aqueous phase on particle diameter.

increased to 2.0 M. When the W/O emulsion prepared under such conditions was poured into the aqueous metal chloride solution, secondary emulsification became unstable and irregular-shaped by-products were formed in a vessel. Probably, the internal aqueous phase and external aqueous phase reacted directly because of breakage of very unstable W/O emulsion. Therefore, it seems that the excessive increase of aqueous solutions concentrations made emulsion unstable and caused a negative effect to the formation of micro-sphere particles.

Ion Exchange of Na and Metal Cation

Figure 3 shows a concentration of Na(I) in sodium silicate (Na_2SiO_3) and metal cation concentrations (Mg(II)) in the external phase during the formation of micro-sphere particles. With the elapse of secondary emulsification time, the concentration of the metal cation decreased gradually, while that of Na(I) increased later than the decrease of the metal cation. At first, the ion exchange reaction between Na and Mg cation occurs by the contact of the metal complex and water droplets existing at the vicinity of the interface between the oil phase and the external aqueous phase. Then, the reaction site of ion exchange moves gradually toward the center of the W/O emulsion droplet. The reaction seems to apparently

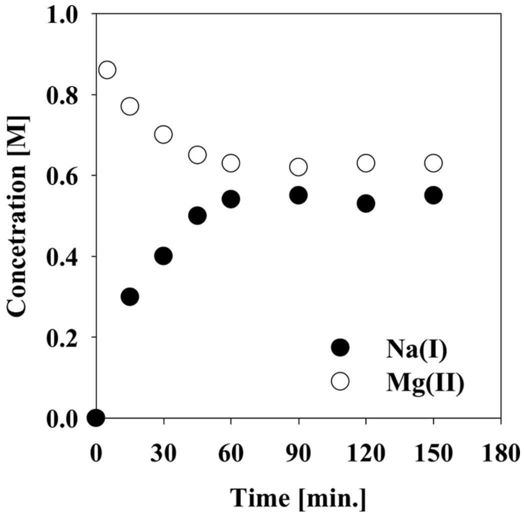


Figure 3. Concentration of Na(I) and Mg(II) in the external phase during the formation of microballons.

stop when the metal cation complex reaches the center of the W/O droplet. Thus, the formation of micro-sphere particles finishes when the ion-exchange reaction reaches a steady state. In this study, taking into account the formation of tight shell, secondary emulsification was continued for 120 min. In the SEM photographs shown in Fig. 1c, the inside of the magnesium silicate micro-sphere particles was filled up. For the formation of hollow in microparticles, the shell-forming process must finish after the growth of the shell having finite thickness. This requires the formation of a tight inorganic shell having low permeability to suppress the internal permeation of metal cation. As a result, shell-formation reaction practically finishes and the inner structure of particle becomes hollow (19). In the case of magnesium silicate, probably because a precipitation reaction is slow and the solubility of magnesium silicate is rather high, the formation of a well-defined reaction front was not established. Consequently, the inner of the particles were partially filled by magnesium silicate.

Kinetic Studies

Preliminary investigations on the rate of uptake of both Ni(II) and Co(II) ions onto prepared Mg-micro-sphere particles indicated that the processes are quite rapid and typically 60–70% of the ultimate adsorption of each ion occurs within the first 20 min of contact. The initial rapid adsorption subsequently gives way to a slow approach to equilibrium, and saturation is reached in about 60 min. The amounts of both Ni(II) and Co(II) adsorbed after each interval time, for a fixed concentration of 0.08 M and at different studied temperatures, are plotted in Fig. 4. The data showed that the amount of Ni(II) and Co(II) adsorbed at

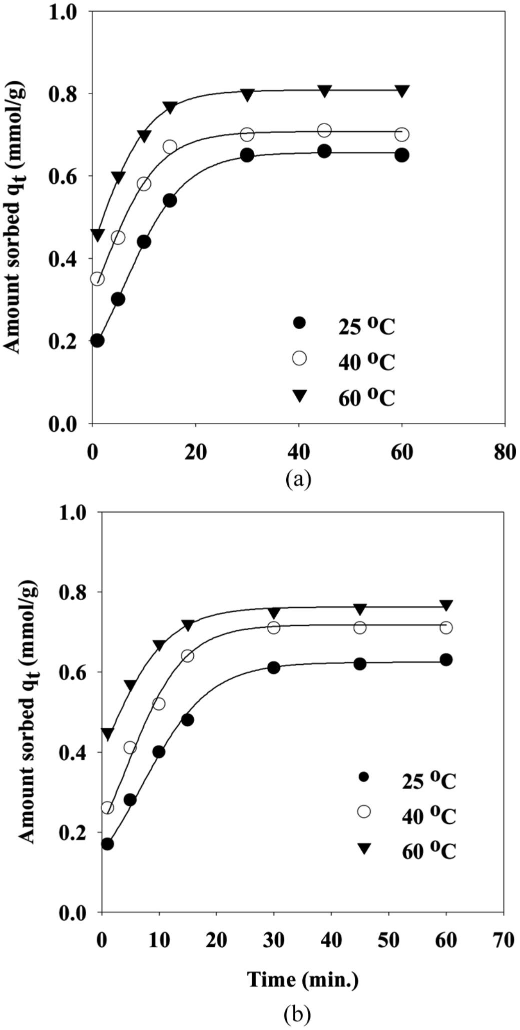


Figure 4. Effect of contact time on the amount adsorbed of (a) Ni(II) and (b) Co(II) from aqueous solution onto Mg-mico-sphere particle. The concentration of metal ion (0.08 M for each metal ion) pH = 5.5, T = 25°C ± 1 weight of micro-sphere = 0.1 g/10 ml.

equilibrium increase with increase in temperature indicating an endothermic nature of the process and the time required to reach saturation remained practically unaffected. It is well recognized that the characteristic of the adsorbent surface is a critical factor that affects the adsorption rate parameters and that diffusion resistance plays an important role in the overall transport of the solute. To describe the changes in the adsorption of the studied ions with time, several kinetic models were tested. The rate constant of each metal ion removal from the solution by Mg-micro-sphere particles was determined using pseudo-first-order and pseudo-second-order rate models. The Lagergren first-order rate expression [20] is written as:

$$\log(q_e - q_t) = \log q_e - k_1\ t/2.303 \tag{2}$$

where q_{e} and q_{t} are the amounts of metal ion adsorbed onto Mg-micro-sphere particles at equilibrium and at time t (mmol/g), respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}). The slopes and intercept of the linear plots of log (q_e−q_{t}) versus t, as shown in Fig. 5, were used to determine the first order rate constant k_1. It was observed that the adsorption of both ions followed the Lagergren equation over the entire range of shaking time explored and the values of the first order rate constants slightly changed with temperature as reported in Table 1. In many cases, the first-order equation of Lagergren does not fit well with

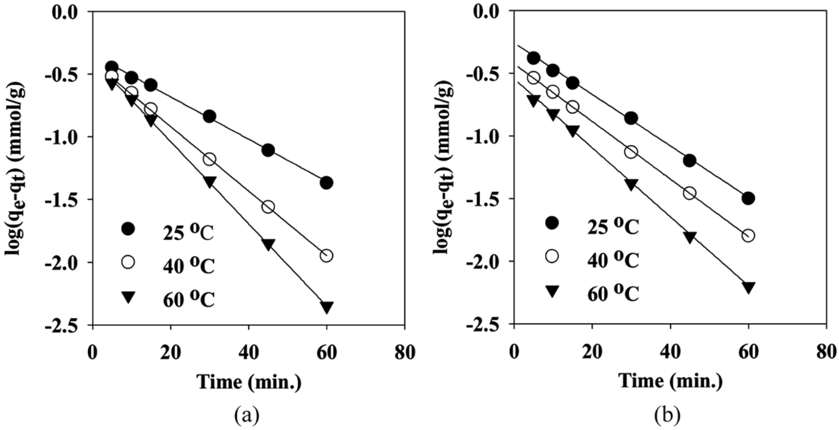


Figure 5. Lagergren plots or the adsorption of (a) Ni(II) and (b) Co(II) from aqueous solutions onto Mg-micro-sphere particles. The concentration of metal ion (0.08 M for each metal ion) pH = 5.5, T = 25°C ± 1 weight of micro-sphere = 0.1 g/10 ml.

Table 1. Pseudo-first order rate constants of Lagergren plots for Ni(II) and Co(II) adsorbed onto Mg-microballoons

	k_1 (min^{-1})		R^2	
Temperature (°C)	Ni(II)	Co(II)	Ni(II)	Co(II)
25	0.050	0.048	0.953	0.941
40	0.055	0.053	0.946	0.928
60	0.066	0.060	0.936	0.943

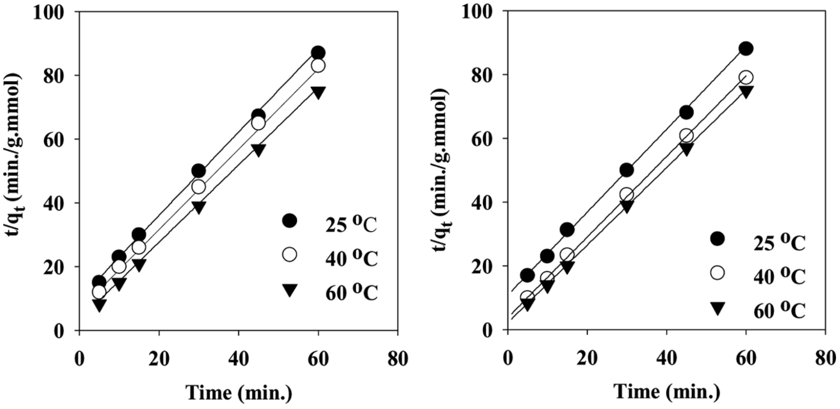
the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (21).

The pseudo-second-order rate model (22) is expressed as:

$$T/q_t = 1/k_2 q_e^2 + 1/q_e\ t \tag{3}$$

where k_2 (g/mmol min) is the rate constant of second-order kinetic model.

The kinetic plots of t/q_t versus t for Ni(II) and Co(II) removal at different temperatures are presented in Fig. 6. The relationship is linear, and the correlation coefficient (R^2), suggests a strong relationship between the parameters and also explains that the process of sorption of each ion follows pseudo-second-order kinetics. The product $k_2 q_e^2$ is the initial adsorption rate represented as $h = k_2 q_e^2$. From Table 2, it can be shown



(a) (b)

Figure 6. Pseudo-second-order kinetic plots for the adsorption of (a) Ni(II) (b) Co(II) ions from aqueous solutions onto Mg-micro-sphere particles.

Table 2. The calculated parameters pseudo-second order rate kinetic models

	q_e (mmol/g)		h (mmol/g min)		k_2 (g/mmol min)		R^2	
Temperature (°C)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)
25	0.65	0.72	0.10	0.09	0.17	0.16	0.994	0.997
40	0.78	0.79	0.25	0.27	0.41	0.53	0.998	0.993
60	0.86	0.89	0.36	0.47	0.48	0.7	0.997	0.995

that the values of the initial adsorption rate 'h' and rate constant 'k_2' are increased with increase in temperature. The correlation coefficient R^2 has an extremely high value (>0.99), and its calculated equilibrium adsorption capacity 'q_e' is consistent with the experimental data. These results suggest that the pseudo second-order sorption mechanism is predominant and that the overall rate constant of each ion appears to be controlled by the chemisorption process (20,21).

Other simplified models are also tested because of the fact that the above two equations cannot give a definite mechanism. It is also known that at an intensive stirring of the adsorptive system, the intraparticle diffusion of the solute sorbed from the solution into the adsorbent pores could be a limiting step. In this study, two models, namely the Weber and Morris models (23) and that suggested by Helfferich (24) were also used. The Morris–Weber equation is written as:

$$q_t = K_{ad} t^{1/2} \tag{4}$$

where K_{ad} is the rate constant of intraparticle transport (mmol/g min$^{1/2}$).

According to this model, plotting a graphic of q_t versus $t^{1/2}$, if a straight line passing through the origin is obtained, it can be assumed that the involved mechanism is a diffusion of the species. In this case the slope of the linear plot is the rate constant of the intraparticle transport. As can be seen in Fig. 7, for times up to 30 min, the Morris–Weber relationship holds good and the values of K_{ad} were calculated, from the slope of the linear plots obtained, and presented in Table 3.

Kinetic data were also analyzed by the procedure given by Helfferich (24). Various parameters were calculated using the following equations as given by Boyd et al. (25).

$$\mathrm{F} = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\exp[-n^2 Bt] \tag{5}$$

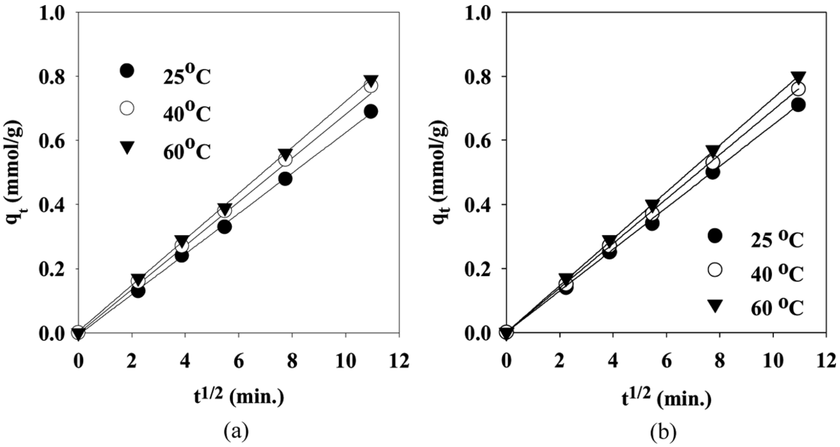


Figure 7. Morris-Weber kinetic plots for the adsorption of (a) Ni(II) and (b) Co(II) ions from aqueous solutions onto Mg-micro-sphere particles.

and

$$B = \pi^2 D_i / r_o^2 \qquad (6)$$

where F is the fractional attainment of adsorption at time t ($F = q_t/q_e$), B is a mathematical function (the slope of Bt vs t plots), D_i is a self-diffusion coefficient of the ions, n is an integer number, refers to the radius (r_o) of the particles.

Bt values for the observed values of F were obtained from Reichenberg's table by using the equation (5) derived by Reichenberg (26):

$$Bt = 2\pi - \pi^2 F(t)/3 - 2\pi[1 - (\pi/3)F(t)]^{1/2} \qquad (7)$$

Table 3. Intraparticle diffusion rate constant for Ni(II) and Co(II) adsorbed onto Mg-microballoons

	K_{ad} (mmol/g min$^{1/2}$)		R^2	
Temperature (°C)	Ni(II)	Co(II)	Ni(II)	Co(II)
25	0.075	0.070	0.998	0.978
40	0.060	0.057	0.995	0.986
60	0.055	0.051	0.996	0.967

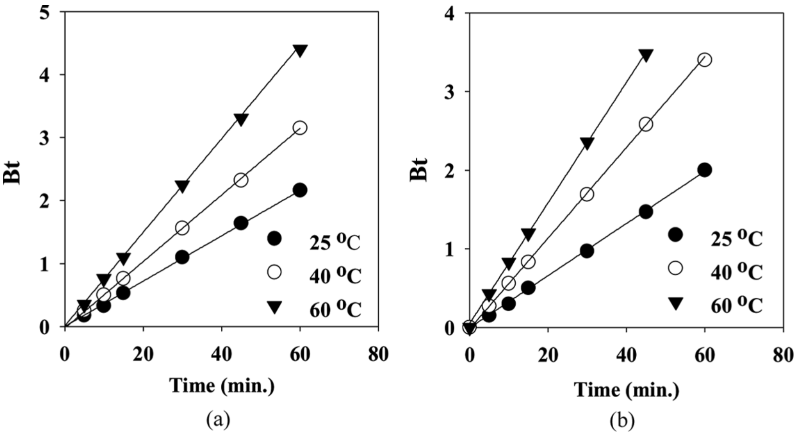


Figure 8. Plots of Bt as a function of time for the adsorption of (a) Ni(II) (b) Co(II) from aqueous solutions onto Mg-micro-sphere particles.

Figures 8a,b depict the Bt versus time plots for Ni(II) and Co(II) at different temperatures. The linearity test of Bt test versus time plots is employed to distinguish between the film and particle diffusion controlled rates of adsorption process. The plots are linear and pass through the origin, indicating the adsorption process to be particle diffusion at all studied temperatures.

Adsorption Isotherms

The adsorption isotherms for the removal of Ni(II) and Co(II) from aqueous solutions onto Mg-micro-sphere particles are shown in Figures 9 and 10. The initial rapid adsorption gives way to a slow approach to equilibrium at higher ion concentrations. These results reflect the efficiency of Mg-micro-sphere particles for the removal of both ions from aqueous solution in a wide range of concentrations. The isotherm parameters were evaluated using the Langmuir and Freundlich isotherm models. The Langmuir isotherm equation could be written as:

$$C_e/q_e = 1/Q_0 b + 1/Q_0 \mathrm{C_e} \qquad (8)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mmol/g), C_e the equilibrium concentration of the solute in the equilibrium solution (mmol/l), Q_0 the monolayer adsorption capacity

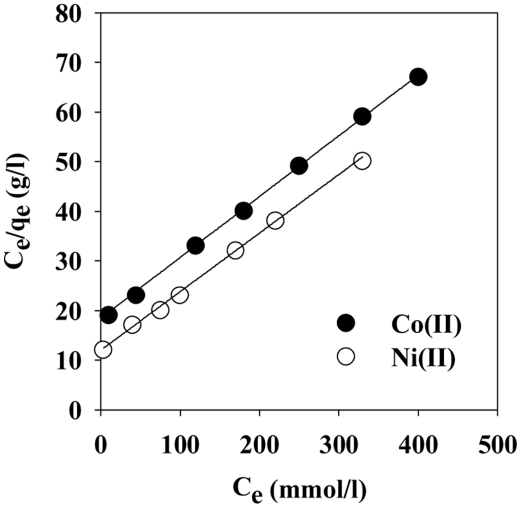


Figure 9. Langmiur isotherm plots for the adsorption of Co(II) and Ni(II) from aqueous solutions onto Mg-micro-sphere particles.

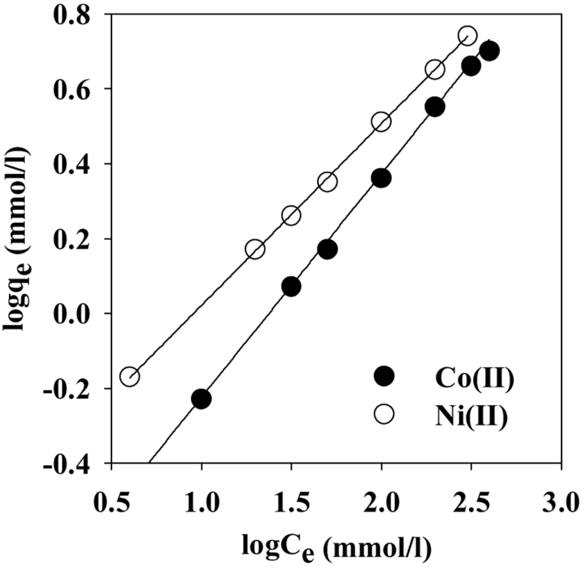


Figure 10. Freundlich isotherm plots for the adsorption of Ni(II) and Co(II) ions from aqous solution onto Mg-micro-sphere particles.

(mmol/g). Q_0 determined from the Langmuir plot, were 8.3 mmol/g and 8.0 mmol/g for Ni(II) and Co(II), respectively. Also, the logarithmic form of the Freundlich equation may be written as:

$$\log q_e = \log K_f + 1/n \log C_e \tag{9}$$

where K_f is a constant indicative of the relative adsorption capacity of the adsorbent (mmol/g) and $1/n$ is the constant indicative of the intensity of the adsorption process. The Langmuir and Freundlich isotherms for the adsorption of the two metal ions on the prepared micro-sphere particles are presented in Figs. 9 and 10, respectively. The straight lines obtained for the two-adsorption isotherms indicate that the adsorption of both ions fit with the two investigated isotherm models. The adsorption intensity (n) for Ni(II) and Co(II) was found to be 2.1, and 1.7, respectively. The value of n lies between 1 and 10, indicating favorable adsorption (27).

In case of Ni(II), the correlation coefficient for Langmuir and Freundlich isotherms were found to equal 1 and 0.989, respectively. The values obtained from these correlation coefficients indicate that the isotherms are best fit with the Langmuir isotherm. Also, in the case of Co(II) the correlation coefficient for Langmuir and Freundlich isotherms were found to equal 0.999 and 0.940, respectively. While the adsorption obtained can fit both Langmuir and Freundlich isotherms, it is to be mentioned that the Langmuir adsorption isotherm is more favored based on the correlation coefficient obtained from the analysis of the data.

CONCLUSION

The present study demonstrated that the Mg-silicate microballoons containing CYANEX923 was successfully formed by ion exchange reaction at the interface between the internal aqueous phase and oil phase. The addition of a proper amount of CYANEX923 made it possible to prepare micro-sphere particles in a short time. From SEM observation of the obtained micro-sphere particles, it was found that micro-sphere particles had a homogeneous shell and particle size. The particle size and shell thickness were ~10 µm and below 2 µm, respectively. The adsorption of Co(II) and Ni(II) from aqueous solutions using prepared micro-sphere particles was investigated. The results of Ni(II) and Co(II) adsorption reported, showed that Mg-silicate micro-sphere particles is an efficient adsorbent media for the removal of Ni(II) and Co(II) from aqueous solutions. Langmuir isotherm model are the best choice to describe the observed equilibrium data. The adsorption of both metal ions is an endothermic process and the results show that Mg-silicate micro-sphere particles can be fruitfully employed for the removal of these metal ions in a wide range of concentrations.

ACKNOWLEDGMENT

My great appreciation and sincere gratitude to Prof. Dr. H.F. Aly, Prof. of Nuclear Chemistry and Chairman of Atomic Energy Authority, previously, for his valuable help and support throughout this work.

REFERENCES

1. El-Nadi, Y.A.; El-Hefny, N.E.; Daoud, J.A. (2007) Extraction of lanthanum and samarium from nitrate medium by some commercial organophosphorus extractants. *Solv. Extr. Ion Exch.*, *25*: 225–240.
2. Reddy, B.R.; Radhika, P.; Kumar, J.R.; Priya, D.N.; Rajgopal, K. (2004) Extractive spectrometric determination of Co(II) in synthetic and pharmaceutical samples using CYANEX923. *Anal. Sci.*, *20*: 345–349.
3. Forsythe, J.H.W.; Magee, R.J.; Wilson, C.L. (1958) The analytical chemistry of the pyridine thiocyanates—I: The separation of cobalt and nickel by solvent extraction. *Talanta*, *1*: 249–251.
4. Gupta, B.; Tandon, S.N.; Deep, A. (2002) Recovery of cobalt and nickel from spent catalysts using CYANEX923. In: *Proceedings of the International Solvent Extraction Conference*, ISEC' 2002, 793–797.
5. Nishihama, S.; Sakaguchi, N.; Hirai, T.; Komasawa, I. (2002) Extraction and separation of rare earth metals using microcapsules containing bis(2-ethylhexyl)phosphinic acid. *Hydrometallurgy*, *64*: 35.
6. Kondo, K.; Kamio, E. (2002) Separation of rare earth metals with a polymeric microcapsule membrane. *Desalination*, *144* (1–3): 249–254.
7. Yang, W.W.; Luo, G.S.; Wu, F.Y.; Chen, F.X.; Gong, C. (2004) Di-2-ethylhexyl phosphoric acid immobilization with polysulfone microcapsules. *Reactive and Functional Polymers*, *61* (1): 91–99.
8. Mimura, H.; Ohta, H.; Hoshi, H.; Akiba, K.; Onodera, Y. (2001) Selective uptake and recovery of palladium by biopolymer microcapsules enclosing Cyanex-302 extractant. *J. Nucl. Sci. Technol.*, *36*: 31.
9. Laguecir, A.; Frère, Y.; Danicher, L.; Burgard, M. (2002) Size, Effect of complexing microcapsules on copper ion extraction. *Europ. Poly. J.*, *38* (5): 977–981.
10. Laguecir, A.; Frere, Y.; Danicher, L.; Burgard, M. (2002) *Eur. Polym. J.*, *38*: 977.
11. Dhruv, K.S.; Srivastava, M. (2005) Selective uptake and recovery of cadmium(II) by microcapsule containing chelating resin. *Sep.Purif. Technol.*, *45* (1): 1–7.
12. Lin, J. (2000) Recent development and applications of optical and fiber-optic pH sensors. *TrAC Trends in Analytical Chemistry*, *19*: 541–552.

13. Yang, W.Y.; Qian, J.W.; Shen, Z.Q. (2004) A novel flocculant of $Al(OH)_3$-polyacrylamide ionic hybrid. *Journal of Colloid and Interface Science*, *273*: 400–405.
14. Kato, T.; Ushijima, H.; Katsumata, M. (2002) Fabrication of hollow alumina microspheres via core/shell structure of polymethylmethacrylate/alumina prepared by mechanofusion. *Journal of Materials Science*, *37*: 2317–2321.
15. Chah, S.; Fendler, J.H.; Yi, J. (2002) Nanostructured gold hollow microspheres prepared on dissolvable ceramic hollow sphere templates. *Journal of Colloid and Interface Science*, *250*: 142–148.
16. Ono, H.; Takahashi, K. (1998) Preparation of silica microparticles by sol-gel method in W/O emulsion. *Journal of Chemical Engineering of Japan*, *31*: 808–812.
17. Marczenko, Z. (1976) *Spectrophotometric Determination of Elements*; Ellis Harwood Ltd.: Poland.
18. Ohtake, T.; Hano, T.; Takagi, K.; Nakashio, F. (1987) Effect of viscosity on drop diameter of W/O emulsion dispersed in a stirred tank. *Journal of Chemical Engineering of Japan*, *20*: 443–447.
19. Gasser, M.S. (2008) Preparation and application of inorganic micro-sphere particles membrane. *Sep.Sci.Tech.*, *43*: 1–13.
20. Lagergen, S.; Seven, Bil. K. (1898) *Vatenskapsakad. Handl.*, 24.
21. McKay, G.; Ho, Y.S. (1999) The sorption of lead(II) on peat. *Water Res.*, *33*: 585–587.
22. Kay, G.; Ho, Y.S. (1999) Pseudo-second order model for sorption processes. *Process Biochem.*, *34*: 451–460.
23. Weber, W.J.; Morris, J.C. (1963) Kinetics of adsorption on carbon from solutions. *J. Sanit. Eng. Div. Am. Soc. Eng.*, *89*: 31.
24. Helfferich, F. (1962) *Ion Exchange*; McGraw Hill: New York.
25. Boyd, G.B.; Andrson, A.W.; Myres, L.S. (1947) The exchange adsorption of ions from aqueous solutions by zeolites. *J. Am.Chem. Soc.*, *69*: 28.
26. Reichenburg, D. (1953) Properties of ion-exchange resin in relation to their structure. III. Kinetics of exchange. *J. Am. Chem. Soc.*, *75*: 589.
27. Mckay, G.; Blair, H.S.; Garden, J.R. (1982) Adsorption of dyes on chitin 1. Equilibrium studies. *J. Appl. Polym. Sci.*, *27*: 3043.