Environmental Engineering and Management Journal
February 2015, Vol.14, No. 2, 449-454
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

ION EXCHANGE PROCESSES ON WEAK ACID RESINS FOR WASTEWATER CONTAINING COOPER IONS TREATMENT

Cristina Modrogan*, **Alexandra Raluca Miron, Oanamari Daniela Orbulet, Cristina Costache, Giani Apostol**

University "Politehnica" of Bucharest, Faculty of Applied Chemistry and Materials Science,
Departament of Analytical Chemistry and Environmental Engineering, 1-7 Polizu Str., Bucharest, Romania

Abstract

The capacity of ion exchange resins, MN 500 and C100 H, for the removal of copper ions from aqueous solution has been investigated under different conditions, namely: initial solution pH, initial metal-ion concentration and contact time.

The adsorption of Cu(II) on these resins follows the first-order reversible kinetic. The film diffusion of Cu (II) in these ion exchange resins was shown to be the main rate limiting step. The studies showed that these cation exchange resins can be used as efficient adsorbent material for the removal of Cu (II) from aqueous solutions. The adsorption process, which is pH dependent, shows maximum removal of copper in the pH range 2-7 for an initial copper concentration of 10 mg/L.

The adsorption rate constants for all these kinetic models have been calculated. Results showed that the intraparticle diffusion and initial Cu(II) sorption into resins was the main rate limiting step. The uptake of copper by the ion exchange resins is reversible and thus has good potential for the removal/recovery of copper from aqueous solutions. After the experiments we concluded that such ion exchange resins can be used for the efficient removal of copper from water and wastewater.

Key words: copper, ion exchange, Purolite MN 500, Purolite C 100 H, sorption capacity

Received: November, 2014; Revised final: February, 2015; Accepted: February, 2015

1. Introduction

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment and air. Copper also occurs naturally in plants and animals. Copper is necessary for good health. It is an essential trace element that facilities the activity of several enzymes. The element provides a role in the development and maintenance of the cardiovascular system, including the heart, arteries and the blood vessels, the skeletal system, and the structure and function of the nervous system, including the brain (Adhoum et al., 2004; Ahmaruzzaman et al., 2011; Basha et al., 2011).

Copper is found in varying amounts in all tissues and about 50 percent of the total copper content of the body are found in the bones and muscles. The highest concentration of copper is found in the brain and liver.

However, very large single or daily intakes of copper can harm human health. Long term exposure to copper dust can irritate the nose, mouth, eyes and cause headaches, dizziness, nausea and diarrhea. Victims of Wilson's disease will steadily accumulate it in the liver, central nervous system and kidneys.

Copper is toxic to aquatic life and certain microorganisms potentially disrupting nutrient cycling processes. Hazards depend upon the form and bio availability of copper (Basha et al., 2011). In order to protect the public health and aquatic life, it is necessary to remove copper from industrial effluent before discharging it to public wastewater treatment plant or receiving waters.

---

* Author to whom all correspondence should be addressed: e-mail: c_modrogan@yahoo.com

The average concentration of copper in ground water is similar to that in lakes and rivers. However, monitoring data indicates that some ground waters contain higher levels of copper. This is generally strongly attached to the particles in the water. Lakes and reservoirs recently treated with copper compounds for algae control or the ones receiving cooling water from a power plant may have high concentrations of dissolved copper. Once in natural water, much of this copper soon attaches to particles or converts to forms that cannot easily enter the body (EPA, 2002; Imamoglu et al., 2008; Kononova et al., 2014; Sousa et al., 2010).

Soil generally contains between 2 and 250 ppm copper, although concentrations close to 7,000 ppm have been found near copper production facilities. High concentrations of copper may be found in soil because dust from these industries settles out of air, or waste from mining and other copper industries are disposed of on the soil.

Copper is quite malleable and good conductor of heat and electricity. In terms of electrical conductivity, only silver is more effective, thus it is used in electrical industry. Copper is widely used in the production of wire, brass, boiler pipe, cooking utensils and fertilizers etc.

The potential sources of pollution with copper are: smelting and refining industries, copper wire manufacturing, coal burning, iron and steel industries, metal cleaning operations, plating baths, rinses and manufacturing of printed circuit. Copper is found in industrial discharge and is used as an algaecide in reservoirs.

Various methods exist for the removal of toxic metal ions from aqueous solutions (Bohdana et al., 2008; Delvaux et al., 2000; Crini et al., 2014; Helfferich et al., 1995; Pollution Databse, 2004; Weber et al., 2008). Ion exchange is widely used and with good performance in the removal and recovery of metals from natural water and industrial wastewater (Fu et al., 2014; Samarghandi et al., 2013). Copper usage and pollution should be reduced wherever possible.

2. Experimental

All chemicals used during experiments were purchased from Merck (Germany). All the experiments conducted were carried out in duplicate sets. All measurements were performed in parallels in each set. The removals reported are the average of the parallel measurements of the duplicate sets and the parallel measurements.

Ion exchange studies were done by contacting synthetic aqueous solutions containing 1 ÷ 100 $mg \cdot L^{-1}$ Cu (II), with an ion exchange resin, in a batch system. In these studies, a strongly basic anion exchanger, sort MN 500 and C 100 H (Purolite – Romania), was used. MN 500 is a hypercrosslinked strong acid resin and C 100 H is a premium gel, polystyrenic, strong acid cation exchange resins. In this paper, the influence of water pH and the exchange anion onto Cu (II) retention kinetic was studied. The solutions containing Cu (II) ions have been prepared using $CuSO_4$ and deionised water. For the adjustment of the pH value, a 1N sulphuric acid solution has been used.

During the kinetic study, aqueous solutions containing 100 $mg \cdot L^{-1}$ were used. Thus, 50 mL of solution were contacted with $1 \pm 2 \cdot 10^{-4}$ g of resin, under batch conditions, at different contact times as follows: 2, 4, 6, 8, 10 and 12 minutes. The temperature control was done using an incubator FOC 225E –Velp Scientifica.

The influence of the exchange ion nature was studied at a pH value of 5 ± 0.2. The pH control was done by using a pH meter Consort C830. The Cu (II) concentration in aqueous phase was determined by the colorimetric method using a spectrophotometer model CINTRA 5.

3. Results and discussion

The H^+/Cu^{2+} ion exchange rates on the gel-like weak acid resin MN 500 and C 100H were measured under conditions favouring a particle diffusion controlled mechanism, namely in concentrated external solutions using an efficient stirring. The experiments were performed at constant temperature (20° C) and two stirring speed (500 and 600 min^{-1}) for different size fractions. The resin was initially in H^+ form, and the outgoing proton in the external solution after replacement by Cu^{2+} ion was monitored with of pH meter at appropriate time intervals, Δt.

The proton activity coefficient is considered constant and the ratio of the activity differences in equation 1 could be taken equal to the ratio of the concentration differences defining the fractional attainment equilibrium.

The pH at time zero was considered as the first value read after the addition $Cu(SO_4)_2$ solution under efficient stirring, varying in the range of 2.7 - 1.8. The ion exchange rate was measured for systems with an external solution of 0.997 M $Cu(SO_4)_2$.

The mean radius of the swollen beads in metal form was measured microscopically. The results are given as the mean of 50 determination ans 99.9 % confidence limits according to Student distribution: $(0.359 \pm 0.025) \times 10^{-3}$, $(0.331 \pm 0.022) \times 10^{-3}$, $(0.294 \pm 0.016) \times 10^{-3}$ for MN 500 and respectively $(0.507 \pm 0.025) \times 10^{-3}$, $(0.502 \pm 0.022) \times 10^{-3}$, $(0.495 \pm 0.016) \times 10^{-3}$ for C 100 H.

The experimental results obtained for H^+/Cu^{2+} ion exchange rate on MN 500 and C 100 H, for different sizes of particles and constantly stirring, are given in Figs. 1 and 2. The experiment show that the decreasing of the mean radius of the swollen beads an increase of the stirring speed on the ion exchange rate within experimental errors. The obtained results support an ion done at different time intervals in order to collect data for the entire range of time of the ion exchange process.

The apparent ion exchange capacity Q_{app}(2) was estimated from the experimental pH at time t = 0 and at equilibrium with Eq. (1), where V_S is the solution volume with correction for swelling, pH_{eq} is the pH at equilibrium, pH_i initial, f_{H+} is the proton activity factor and $m_{\text{sat resin}}$ is the mass of resin saturated with water vapours (g).

$$Q_{app} = \frac{V_s\left(10^{-pH_{eq}} - 10^{-pH_i}\right)\cdot f_{H^+}}{m_{\text{sat resin}}} \tag{1}$$

For the H^+/Cu^{2+} ion exchange process on MN 500 and C 100 H in concentrated external solution (0.997 M) at 20° C, the degree of dissociation, γ, of the weak acid functional groups and the apparent ion exchange capacity, Q_{app}, were evaluated using the Eqs. (2, 3). The results are given in Table 1.

Several kinetic functions were fitted to the experimental *F vs. t* curves. The best fit was selected for the highest coefficient of determination and F-statistic parameters of the goodness of fit, and has the physical meaning of an empirical kinetic equation. For all the experiments for this system the best fitted function was the empirical Eq. (3).

$$F = a(1-\exp(-bt)) + c[(1-1/(1+cdt))] \tag{2}$$

Table 2 gives the coefficients of the empirical ecuation 3 for H^+/Cu^{2+} ion exchange process on MN 500 and C 100 H resin for different size fraction, at 500 min^{-1} and 20°C. The empirical kinetic equations were used to interpolate points for F → 0, to calculate the interdiffusion coefficients also at low fraction of exchange.

In order to verify which mechanism describe better the experimental points the Eq. (3) for film diffusion control, the experimental data for H^+/Cu^{2+} ion exchange kinetics on a weak acid resin were also used for modeling, were F is the fractional attainment of equilibrium at time t and $k = -3DC/R\delta\overline{C}$; C – the molar concentration of the external solution; $\overline{C}$ - the molar concentration of fixed ionic groups, D – the interdiffusion coefficient in the film, R – the mean radius of the swollen resin beads, δ - the thickness of the Nernst film of liquid phase.

$$n(1-F) = -k\cdot t \tag{3}$$

The results presented in Figs. 3 and 4 showed that the hypothesis of film diffusion mechanism is not supported by the experimental data.

The intraparticle integral interdiffusion coefficients were obtained with quasi-homogeneous resin phase kinetic models. The H^+/Cu^{2+} integral interdiffusion coefficients were calculated for different fractional attainment of equilibrium using Eqs. (4 – 8). Knowing the time t for the considered F, and the mean radius of the swollen resin particles, the diffusion coefficient $\overline{D}$ can be calculated. The convergence of series 4 and 6 was considered to be achieved when the difference between two consecutive values of $\overline{D}$ was equal to or smaller than 0.1%. The results are presented in Figs. 3 - 6. All experiments were performed for ù<0.1, justifying the use of both ISV and FSV conditions.

In Figs. 3 and 4 it is presented the variation of H^+/Cu^{2+} integral interdiffusion coefficients on MN 500 and C 100 H resin, calculated with Eq. (4), n =10 and the simplified Eqs. of Reichenberg, (4) and (5) (Reichenberg, 1953).

$$F(t) = 1 - \frac{\overline{Q}_A(t)}{\overline{Q}_A^0} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\overline{D}t\pi^2 n^2}{r_0^2}\right) \tag{4}$$

$$F(t) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2\tau\right)$$

where $\overline{Q}_A(t)$ is the amount of A in the exchanger at time t; $\overline{Q}_A^0$ - the initial amount of A in the ion exchanger; $F(t)$ is the fractional attainment of equilibrium, defined by $F(t) \equiv \frac{\left(\overline{Q}_A^0 - \overline{Q}_A(t)\right)}{\left(\overline{Q}_A^0 - \overline{Q}_A^\infty\right)}$; $\overline{Q}_A^\infty$ - the amount of A left in the exchanger when equilibrium is attained.

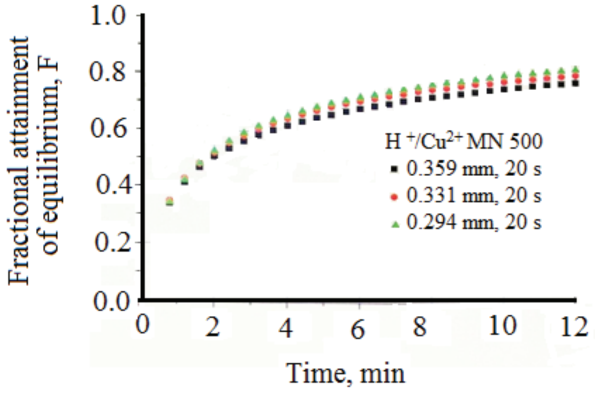

Fig. 1. Fractional attainment of equilibrium vs. time for H^+/Cu^{2+} ion exchange process on MN 500; 20°C; 0.997 M Cu $(SO_4)_2$; 500 min^{-1}.

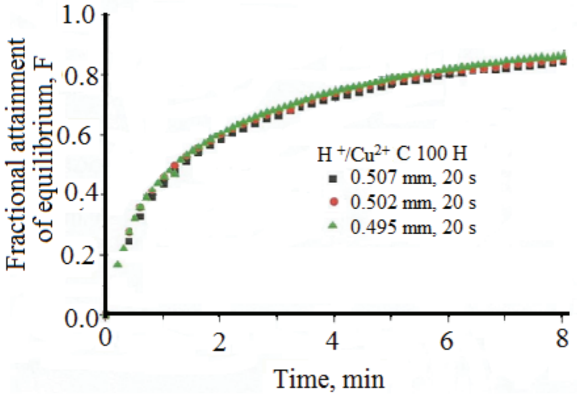

Fig. 2. Fractional attainment of equilibrium vs. time for H^+/Cu^{2+} ion exchange process on C 100 H resin ; 20°C; 0.997 M Cu $(SO_4)_2$; 500 min^{-1}.

Table 1. Experimental and theoretical evaluations of the apparent ion exchange capacity and the degree of dissociation of the weak acid resin MN 500 and C 100 H for H^+/Cu^{2+} ion exchange; 20℃

$R\cdot10^{-3}$ (m)	*Resin mass (g)*	*Vs (L)*	*pH_i*	*pH_{eq}*	*μ mol/L*	*Moisture %*	*[X] mol/L*	*Q_{app} exp. (meq/g)*	*Q_{app} calc. (meq/g)*	*γ exp.*	*γ calc.*
MN 500											
0.359	0.9630	0.05	2.70	1.80	1.495	51.0	11.55	0.653	0.116	0.056	0.011
0.359	1.0548	0.05	2.51	1.80	1.495	51.0	11.55	0.541	0.116	0.046	0.011
0.359	1.0501	0.05	2.50	1.80	1.495	51.0	11.55	0.526	0.111	0.046	0.011
0.359	1.0236	0.05	2.71	1.80	1.495	51.0	11.55	0.578	0.115	0.050	0.011
0.359	1.0312	0.05	2.41	1.78	1.495	51.0	11.55	0.510	0.116	0.040	0.011
0.331	0.9612	0.05	2.65	1.77	1.495	51.7	12.01	0.639	0.117	0.052	0.010
0.331	0.9910	0.05	2.34	1.80	1.495	51.7	12.01	0.505	0.119	0.038	0.011
0.331	0.9624	0.05	2.68	1.80	1.495	51.7	12.01	0.590	0.121	0.050	0.011
0.331	1.0080	0.05	2.42	1.78	1.495	51.7	12.01	0.510	0.117	0.038	0.011
0.331	0.9676	0.05	2.66	1.80	1.495	51.7	12.01	0.590	0.120	0.048	0.011
0.294	0.7961	0.05	2.70	1.83	1.495	51.5	11.35	0.666	0.120	0.058	0.011
0.294	0.5974	0.05	2.50	1.88	1.495	51.5	11.35	0.70	0.126	0.061	0.011
C 100 H											
0.507	1.0562	0.05	2.70	1.80	1.120	51.0	11.55	0.198	0.184	0.0176	0.015
0.507	1.2340	0.05	2.56	1.80	1.120	51.0	11.55	0.216	0.192	0.0181	0.015
0.507	0.9034	0.05	2.65	1.80	1.120	51.0	11.55	0.216	0.192	0.0181	0.015
0.507	1.0610	0.05	2.41	1.78	1.120	51.0	11.55	0.215	0.178	0.0180	0.015
0.507	0.9000	0.05	2.58	1.88	1.120	51.0	11.55	0.233	0.190	0.0191	0.015
0.502	1.0162	0.05	2.68	1.83	1.120	51.0	11.55	0.212	0.185	0.0179	0.015
0.502	1.0429	0.05	2.60	2.281	1.120	51.0	11.55	0.217	0.180	0.0186	0.015
0.502	1.0701	0.05	2.55	1.88	1.120	51.0	11.55	0.210	0.183	0.0183	0.015
0.502	1.0664	0.05	2.65	1.80	1.120	51.7	12.01	0.210	0.191	0.0171	0.014
0.502	1.0664	0.05	2.70	1.78	1.120	51.7	12.01	0.210	0.192	0.0171	0.014
0.495	1.0616	0.05	2.70	1.80	1.120	51.7	12.01	0.218	0.194	0.0178	0.014
0.495	1.0810	0.05	2.42	1.83	1.120	51.5	11.35	0.211	0.181	0.0178	0.015

Table 2. The coefficients of the empirical equation 3 on F vs. t experimental curves for H^+/Cu^{2+} ion exchange process on weak acid resin MN 500 and C 100 H

R (mm)	*No. of exp. Points*	*a*	*b*	*c*	*d*	*Coef. det.*	*F statistic*
MN 500							
0.359	284	0.632±0.040	0.046±0.008	0.388±0.031	0.007±0.0008	0.9968	22496
0.331	280	0.584±0.050	0.068±0.020	0.477±0.050	0.00666±0.0005	0.9966	40340
0.294	200	0.742±0.030	0.033±0.004	0.344±0.015	0.0037±0.0005	0.9974	21787
C 100 H							
0.507	300	0.653±0.030	0.054±0.003	0.446±0.030	0.147±0.023	0.9975	38744
0.502	290	0.737±0.040	0.073±0.003	0.561±0.040	0.291±0.087	0.9949	47571
0.495	158	0.930±0.043	0.044±0.001	0.462±0.044	1.9e+5	0.9988	21812

The fractional attainment of equilibrium *F(t)* depends only on the magnitude of the dimensionless time parameter $\tau = \frac{\overline{D}t}{r_0^2}$. When $\frac{\overline{D}t}{r_0^2}$ is small, the series 6 does not converge rapidly. In the range *F(t)*<0.85, Reichenberg (Reichenberg, 1953) introduces the approximation (Eq. 5):

$$F(t) = \frac{6}{\pi^{3/2}}(Bt)^{1/2} - \frac{3}{\pi^2}(Bt), \text{ where } B = \frac{\overline{D}\pi^2}{r_0^2} \qquad (5)$$

$$F(t) = \frac{6}{\pi^{3/2}}(\pi^2\tau)^{1/2} - \frac{3}{\pi^2}(\pi^2\tau)$$

For *F(t)* >0.6 Reichenberg's had shown that (Eq. 6):

$$F(t) = 1 - \frac{6}{\pi}exp(-Bt) \qquad (6)$$

Less accurate than Eq. (4), but more convenient for practical use is Vermeulen's approximation (Vermulen, 1953) which fits the whole range 0≤*F(t)*≤1 (Eq. 7):

$$F(t) \cong \left[1 - exp\left(-\frac{\overline{D}\pi^2 t}{r_0^2}\right)\right]^{1/2} \qquad (7)$$

Eqs. (7) for (10) terms is not convergent when ***F*** < 0.1. The mean radius of the swollen resin particles in H^+ form is higher than that in Cu^{2+} form. The size of the particles varies during the ion exchange process from the value corresponding to H^+ form to that in the Cu^{2+} form.

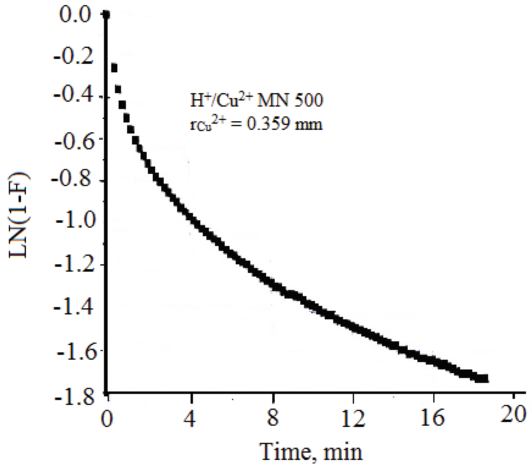

Fig. 3. Testing of the model for film diffusion controlled kinetic on H^+/Cu^{2+} ion exchange process on MN 500 at 20°C; 500 min^{-1}

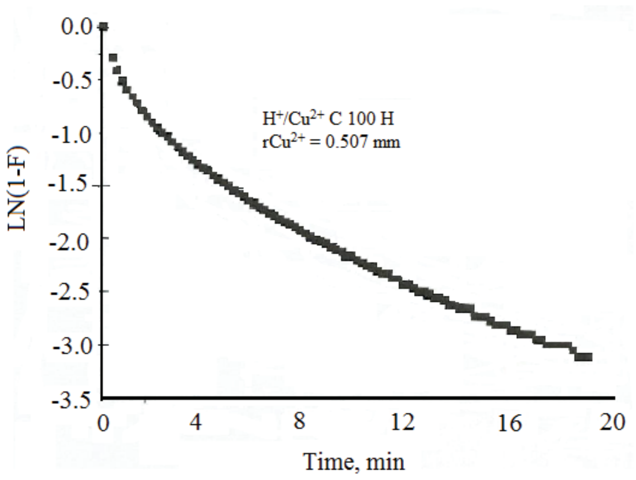

Fig. 4. Testing of the model for film diffusion controlled kinetic on H^+/Cu^{2+} ion exchange process on C 100H at 20°C; 500 min^{-1}

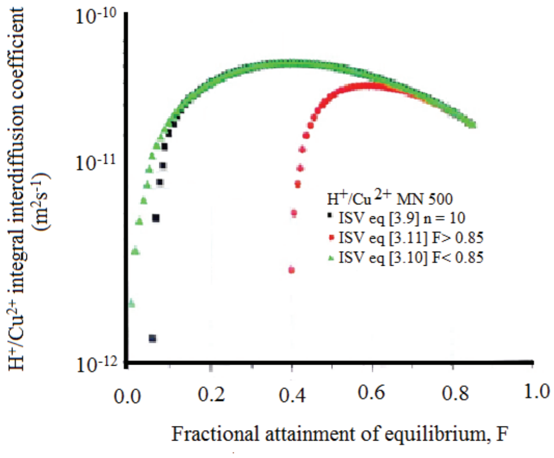

Fig. 5. The H^+/Cu^{2+} integral interdiffusion coefficients vs. fractional attainment of equilibrium calculated with QHRP models; 20°C; 0.359 mm; 500 min^{-1} (MN 500)

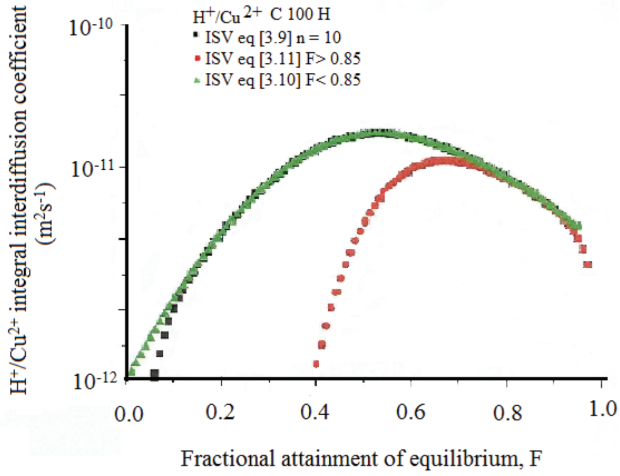

Fig. 6. The H^+/Cu^{2+} integral interdiffusion coefficients vs. fractional attainment of equilibrium calculated with QHRP models; 20°C; 0.507 mm; 500 min^{-1} (C 100 H)

The H^+/Cu^{2+} integral interdiffusion coefficients were calculated with Eq. 8 for all size *fractions* using the mean radii of the swollen resin particles in H^+ and Cu^{2+} forms, being reported in Figs. 5 and 6.

$$F(t)=\frac{\omega+1}{\omega}\left\{1-\frac{1}{\alpha-\beta}\left[\begin{array}{l}\alpha\exp(\alpha^2\tau)(1+erf\alpha\tau^{1/2})-\\ \beta\exp(\beta^2\tau)(1+erf\beta\tau^{1/2})\end{array}\right]\right\} \quad (8)$$

where α and β are the roots of the equation $x^2+3\omega x-3\omega=0$ and erf is the error function.

It can be observed that the variation of the radius beads from H^+ to Cu^{2+} form produces a small variation of the values of the interdiffusion coefficients, for the same size fractions. The interdiffusion coefficients decrease if the size fractions decreases supporting a higher resistance to diffusion in small particles compared with larger ones due to a higher degree of cross linking in small particles.

The H^+/Cu^{2+} integral interdiffusion coefficients increase with the fractional attainment of equilibrium according to the Helfferich minority rule.

4. Conclusions

The present paper was devoted to the investigation of ion exchange kinetics of systems important in waste water treatment on a weak acid gel-like resin with significantly importance in industrial packed bed applications. The investigated systems were H^+/Cu^{2+} on Purolite MN 500 and C 100H. The ion exchange rates were measured in batch systems using a potentiometric method. A procedure diminishing the interference of the electrolyte desorbtion during the measurement of the ion exchange rate was established.

The experiments were perfomed in conditions favouring a particle diffusion controlled mechanism. The kinetic measurements were done for each system for different size fractions of the resin and different stirring speeds in order to assign the ion exchange mechanism. The results support for all the investigated systems an ion exchange mechanism in which the ion interdiffusion inside the resin particle is the controlling step. The value of the interdiffusion coefficients inside the ion exchangers are influenced by many factors sometimes in opposite ways, with different magnitudes and it is very difficult to predict their variation in the given conditions. The integral interdiffusion coefficients calculated with Paterson approximation are in very good agreement with those obtained with the rigorous analytical solution for FSV and avoids the convergence problem and can be used to compute values for integral interdiffusion coefficients for F <0.1.

The results obtained with the simplified equation proposed by Reichenberg for F = 0.85 are in very good agreement with those obtained with the rigorous analytical solution for ISV and avoid the problem of the series convergence.

The H^+/Cu^{2+} interdiffusion coeffeicients on the weak acid resin are not very well discriminated by the resin matrix of the different size fractions, having close numerical values, probably due to the close values for the radius of the hydrated ion in the resin phase.

$\overline{D}_{H^+/Cu^{2+}}$ on C 100 H > $\overline{D}_{H^+/Cu^{2+}}$ MN 500.

Acknowledgements
The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398.

References

Aber S., Ayoubi-Feiz B., Salari D., (2013), Investigation of isothermal and fixed-bed column sorption of Cu (II) onto almond shell, *Environmental Engineering and Management Journal,* **12,** 3, 435-441

Adhoum N., Monser L., Bellakhal N., Belgaied J.E., (2004), Treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and Cr^{6+} by electrocoagulation, *Journal of Hazardous Materials,* **112**, 3, 207-213,

Ahmaruzzaman M., (2011), Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, *Advances in Colloid and Interface Science*, **166**, 36-59

Anis M., Haydar S., Bari A.J., (2013), Adsorption of lead and copper from aqueous solution using unmodified wheat straw, *Environmental Engineering and Management Journal*, **12**, 11, 2117-2124

Basha A.C., Somasundaram M., Kannadasan T., Lee C.W., (2011), Heavy metals removal from copper smelting effluent using electrochemical filter press cells, *Chemical Engineering Journal,* **171**, 563-571

Bensacia N., Fechete I., Moulay S., Debbih-Boustila S., Boos A., Garin F., (2014), Removal of cadmium (II) from aqueous media using cooh/tud-1 mesoporous solid. Kinetic and thermodynamic studies, *Environmental Engineering and Management Journal*, **13**, 10, 2675-2686

Bohdana C., Cantea D.S., Dale J.A., Pincovschi E., Oancea AMS., (2008), Polymeric ion exchangers based on styrene-divinylbenzene matrix. Textural and structural modifications after grafting different functional groups, *Proceedings IEX Cambridge*, 427-434

Crini G., Morin-Crini N., Fatin-Rouge N., Déon S., Fievet P., (2014), Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan, *Arabian Journal of Chemistry*, doi:10.1016/j.arabjc.2014.05.020.

Delvaux B., Kruyts N., Cremers A., (2000), Rhizosphere mobilization of radiocesium in soils, *Environmental Science and Technology,* **34**, 1489-1493

Fu L., Shuang C., Liu F., Li A., Li Y., Zhou Y., Song H., (2014), Rapid removal of copper with magnetic poly-acrylic weak acid resin: Quantitative role of bead radius on ion exchange, *Journal of Hazardous Materials*, **272**, 102–111.

Helfferich F., (1995), *Kinetics, Ion Exchange*, Dover Publications INC., New York, 250-319.

Imamoglu M., Tekir O., (2008), Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks, *Desalination*, **228**, 108-113.

Kononova O.N., Kuznetsova M.A., Mel’nikov A.M., Karplyakova N.S., Kononov Y.S., (2014), Original scientific paper Sorption recovery of copper (II) and zinc (II) from chloride aqueous solutions, *Journal of the Serbian Chemical Society,* **79**, 1037–1049.

Oancea A.M.S., Drinkal C., Höll W.H., (2008), Evaluation of exchange equilibria on strongly acidic ion exchangers with gel, -type, macroporous and macronet structure, *Reactive and Functional Polymers,* **68**, 492-506

Pollution Databse, (2004), Copper and its compounds, European Pollutant Emission Register, On line at: http://pollution.unibuc.ro/?substance=20.

Reichenberg D., (1953), Properties of ion-exchange resins in relation to their structure, III: Kinetics of exchange, *Journal of the American Chemical Society*, **75**, 596

Samarghandi M.R., Zarrabi M., Amrane A., Soori M.M., Sepehr M.N., (2013), Removal of acid black dye by pumice stone as a low cost adsorbent: kinetic, thermodynamic and equilibrium studies, *Environmental Engineering and Management Journal*, **12**, 2137-2147.

Sousa F.W., Oliveira A.G., Ribeiro J.P., Rosa M.F., Keukeleire D., Nascimento R.F., (2010), Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology, *Journal of Environmental Management,* **9**, 1634-1640

Weber V., Popescu A.R., Oancea AMS., (2008), Interdiffusion coefficients in gel and macroporous weak acid resins, *Revista de Chimie*, **59**, 5, 519-524.

Yahaya N.K.E.M., Abustana I., Latiff M.F.P.M., Bello O.S., Ahmad M.A., (2011), Fixed-bed column study for Cu(II) removal from aqueous solutions using rice husk based activated carbon, *International Journal of Engineering & Technology,* **11**, 186-190.