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Effect of the solid/liquid ratio on zinc and cadmium uptake on natural and iron-modified zeolite - Batch scale design

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Zinc and cadmium uptake on natural (NZ) and iron-modified zeolite (IMZ) has been investigated through the two sets of experiments, first one with varying S/L ratios at a constant initial metal concentration and second one with different initial metal concentrations at a single S/L ratio. Results confirm the importance of choosing an optimum S/L ratio in achievement of the maximum removal efficiency with the lowest zeolite mass. Two different methods for the design of batch reactor have been applied to overcome the effect of the S/L ratio. The first approach applied the operating line method with the Dubinin-Radushkevich isotherm, and the second one applied the Rayleigh's method of dimensional analysis. The excellent agreement between predicted and experimentally obtained results for the amount of metal removed per gram of zeolite as well as error functions confirm the applicability of both methods in the batch scale design independently of the S/L ratio.

Keywords: Cadmium, Dimensional analysis, Iron-modified zeolite, Natural zeolite, Reactor design, Zinc

Industrial effluents contaminated with heavy metals pose a significant threat to human health and to the environment, especially in water ecosystems in which they tend to accumulate in organisms, causing diseases and disorders[1,2]. The environmental impact has led to the enforcement of stringent standards of their discharge to the maximum allowable limits. Conventional methods of heavy metal removal from wastewater, such as chemical precipitation or chemical oxidation/reduction are insufficiently efficient at low metal concentrations and generate a toxic metal-bearing sludge which is extremely difficult to dispose of [3-5]. Advanced methods such as ion exchange and membrane technique, are often cost-demanding. Therefore, a search for alternative technologies for metal sequestering up to environmentally acceptable levels is highly required. The ability of natural and chemically modified zeolites to remove metal ions has received considerable attention in the development of these technologies[6-10].

Batch experiments are generally used to determine isothermal sorption characteristics. The most common method used to obtain isotherm parameters is to conduct the equilibrium studies at different solution volumes or at different sorbent mass or by varying the initial concentrations[11]. The effect of the S/L ratio on the sorption efficiency of metal cations on the sorbent is an important parameter to be considered in the adsorber design. The graphical method with an operating line is recognized as an efficient method for reducing the metal solution concentration for the given volume of wastewater by using the minimal amount of sorbent to obtain the desired sorption efficiency. In other words, the design is focused on the determination of an optimum S/L ratio. Under ideal saturation conditions, the S/L ratio should not affect on the amount of sorbed metals per unit of sorbent. However, Puls *et al.*[12] have shown that the sorption of organic and inorganic pollutants is dependent on the S/L ratio to some degree and on the competition system of the mixture.

Also, many studies have confirmed that the sorption constant varies with varying S/L ratios. This anomalous phenomenon is known as the "sorbent concentration effect"[13,14]. The applied sorption models provide a proper description of sorption characteristics only at a specific S/L ratio, and cannot adequately predict the effect of the S/L ratio on sorption properties[15-18]. Scientists have been trying to solve the effect of the S/L ratio by proposing different models[13,14,18-20]. Chang and Wang[15] have proposed the application of the Rayleigh's method of dimensional analysis in the assessment of sorbent-water (S/W) ratio effect on adsorption on the different sorbents and sorbates in the paddy soils moisture regime[15].

The aim of this paper is to investigate the effect of the S/L ratio on zinc and cadmium uptake on natural and iron-modified zeolites. The batch scale design was performed by using the graphical method with the operating line and the Rayleigh's method of dimensional analysis.

Experimental Section

Sample preparation

The natural zeolite (NZ) originated from the Zlatokop deposit, Vranjska Banja, Serbia. The sample was milled and sieved to the particle size fractions of 0.6-0.8 mm. After rinsing and drying at 60°C, the sample was stored in a desiccator.

The iron-modified zeolite (IMZ) was prepared from NZ according to the procedure published previously[21]. The natural zeolite sample was treated separately in three stages: in aqueous solutions of $Fe(NO_3)_3 \cdot 9 H_2O$ prepared in acetate buffer at *p*H=3.6, followed by NaOH and $NaNO_3$ solutions. The prepared IMZ was dried for 24 hours at 40°C, and kept in a desiccator until use. The chemical analysis of natural and iron-modified zeolite was performed by means of classical chemical analysis of aluminosilicates, and Table 1 shows the results.

Physical and chemical characterisation of NZ and IMZ is described in detail in a paper previously published and shows that the modification has no effect on the mineralogical composition (XRD) and structural changes (SEM, FTIR, TG-DTG) while causing changes in the composition of exchangeable cations and physical properties on the zeolite surface[21]. Namely, the modification results in the increase of the negative charge on the IMZ particle surface, which is confirmed by determination of the point of zero charge and the resulting charge is compensated by sodium ions (Table 1). Thus, high sorption efficiency is explained by the individual steps of the modification procedure. The role of treatment with $Fe(NO_3)_3$ in an acetate buffer at *p*H=3.6 was to bind the iron cationic species onto the negative zeolite surface. The NaOH solution was used to initiate hydrolysis of iron cation species bound on the zeolite surface, which became carriers of the negative charge. The basic conditions also caused the deprotonation of $\equiv$Si-OH-Al$\equiv$ zeolite surface groups, which also contributed to the increase of the negative zeolite surface charge. Both steps of the modification procedure are responsible for the enhanced metal sorption, due to the increase in the negative surface charge of the iron-modified zeolite sample which is compensated by exchangeable sodium ions.

Isothermal zinc and cadmium ions sorption in batch experiments at varying S/L ratios

Examinations of zinc and cadmium sorption on NZ and IMZ were performed by using an incubator shaker in the period of 48 h at the room temperature. Different amounts of both zeolite samples, in the range from 0.25 g to 12.00 g (S/L = 2.5; 5; 10; 15; 20; 25; 30; 40; 60; 80; 100; 120 g/L) for zinc sorption and in the range from 0.25 g to 10.00 g (S/L = 2.5; 5; 10; 15; 20; 30; 60; 80; 100 g/L) for cadmium sorption, were shaken with 100 mL of aqueous solutions with the initial concentration of 217.94 mg Zn/L or with 333.63 mg Cd/L. The solutions were prepared by dissolving $Zn(NO_3)_2 \cdot 6 H_2O$ and $Cd(NO_3)_2 \cdot 4 H_2O$ in ultrapure water. The initial *p*H of solution was 4.92 for zinc and 5.89 for cadmium, respectively. After equilibration, *p*H was measured, the suspensions were filtered and concentrations of remaining zinc and cadmium ions as well as released exchangeable cations (Na, K, Ca, Mg) were determined by means of ion chromatography.

Isothermal zinc and cadmium ions sorption in batch experiments at single S/L ratio

Examinations of zinc and cadmium sorption on NZ and IMZ at a single solid-to-liquid (S/L) ratio, S/L = 10 g/L, were performed by shaking 1.000 g of zeolite samples with 100 mL of metal aqueous solutions with initial concentrations in the range 129.30-868.57 mg Zn/L and 233.36-1567.22 mg Cd/L. After 48 h of equilibration, *p*H was measured and concentrations of remaining zinc and cadmium in supernatants were determined using ion chromatography.

Results and Discussion

The effect of the solid/liquid (S/L) ratio

The S/L ratio is an important parameter which determines the capacity of a sorbent for a given initial

Table 1 — Chemical composition of zeolite samples.

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Loss of ignition
NZ	65.40	14.00	2.16	3.56	0.85	1.10	1.50	0.32	11.09
IMZ	62.80	13.90	2.22	3.85	0.80	0.94	3.68	0.17	11.56

concentration of metal ions at the operating conditions. Based on the results of equilibrium concentrations obtained at a single and at varying solid/liquid (S/L) ratios, the removal efficiency, α and amounts of zinc and cadmium uptake per gram of zeolite, q_e have been calculated according to equations:

$$\alpha = \frac{(c_o - c_e)}{c_o} \cdot 100 \qquad ...(1)$$

$$q_e = (c_o - c_e) \cdot \frac{V}{m} \qquad ...(2)$$

where α is the removal efficiency (%), c_o is the initial metal concentration (mg/L), c_e is the equilibrium metal concentration (mg/L), q_e is the the sorbed amount of metal ion per unit mass of zeolite (mg/g), V is the solution volume (L) and m is the zeolite mass (g).

Figure 1a and b shows the graphical dependence of the removal efficiency, α and the amount of zinc and cadmium uptake per gram of NZ and IMZ, q_e at varying S/L ratios and Fig. 1c and d at single S/L ratio.

It is evident that the removal efficiency, α increases with the increasing S/L ratio for both metals. For IMZ, it is higher than 93% at S/L > 20 g/L, while for NZ the removal efficiency it is only 70% at S/L > 80 g/L (Fig. 1a and b). This justifies the modification of NZ because higher removal efficiency is achieved with a smaller mass of IMZ.

The amount of zinc and cadmium removed per gram of NZ and IMZ decreases with the increasing S/L ratio. According to Abd El-Latif *et al.*[22] many factors contributes to this zeolite concentration effect. Among them the most important are remaining unsaturated sorption sites with the increasing S/L ratio. The highest value of q_e for zinc was obtained at S/L ratios up to 5 g/L for both zeolite samples. With a further increase of the S/L ratio, a rapid decrease of q_e values is observed for IMZ, while they continuously

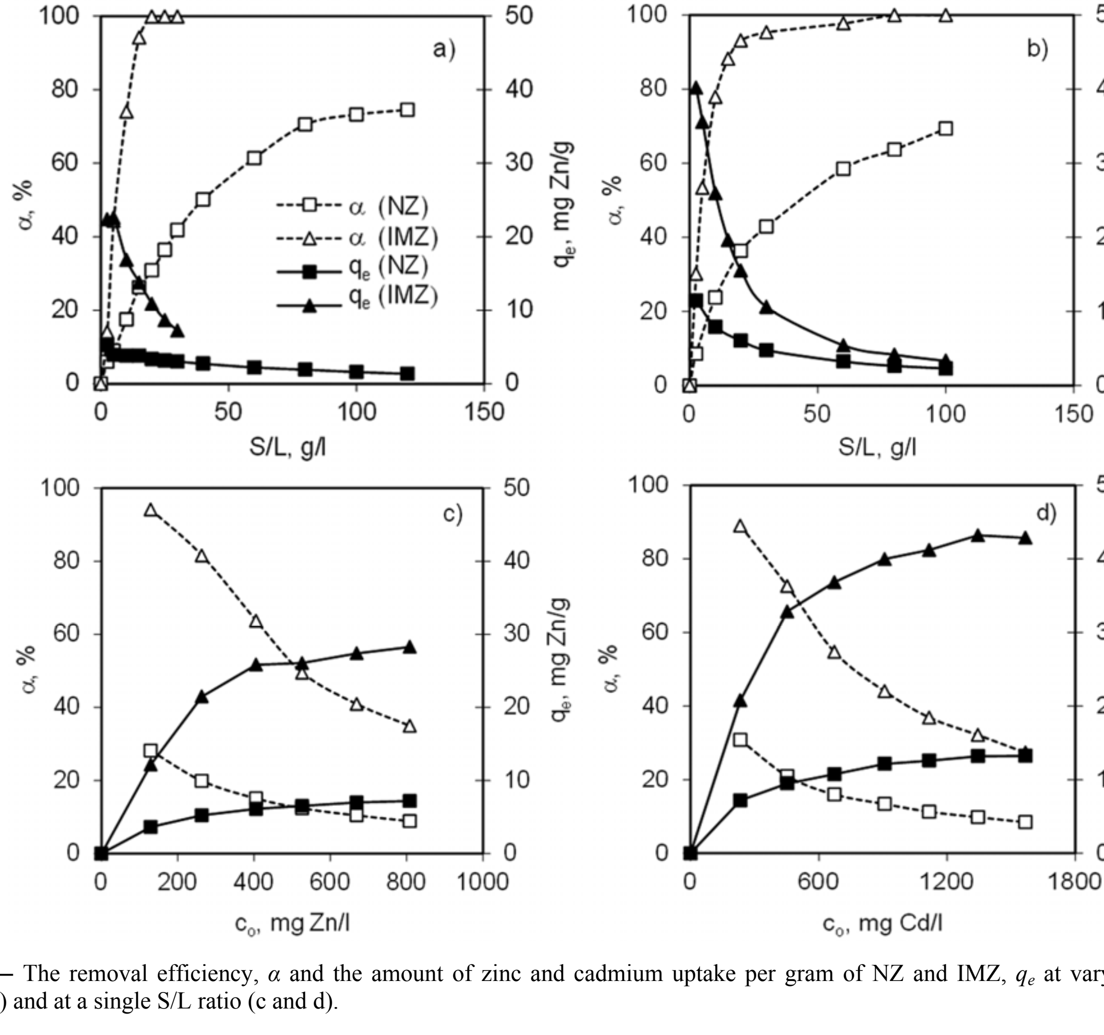

Fig. 1 — The removal efficiency, α and the amount of zinc and cadmium uptake per gram of NZ and IMZ, q_e at varying S/L ratios (a and b) and at a single S/L ratio (c and d).

decrease for NZ. Similar results have been observed for cadmium.

Figure 1c and d shows the removal efficiency, α and the amount of zinc and cadmium uptake per gram of NZ and IMZ, q_e at the single S/L ratio = 10 g/L. The results indicate decreased removal efficiency and increased amount of zinc and cadmium removed per gram of NZ and IMZ with increasing initial concentrations of solutions. This indicates the opposite behaviour of α and q_e at a single and at varying S/L ratios (comparison Fig. 1a and b with Fig. 1c and d).

Sorption isotherm at a single and at varying S/L ratios

Sorption isotherms of zinc and cadmium expressed as the amount of zinc and cadmium uptake per gram of zeolite, q_e versus the equilibrium metal concentration c_e at a single S/L ratio are shown in Figure 2a, and at varying S/L ratios in Figure 2b.

Figures 2a and 2b show the increase of q_e with increasing equilibrium concentration c_e, at a single and at varying S/L ratios. Isotherm curves at a single S/L ratio are stretched and reach a plateau. Reaching a plateau allows for determination of the working capacity and they equal 28.282 mg Zn/g of IMZ, 7.190 mg Zn/g of NZ, 42.876 mg Cd/g of IMZ and 13.239 mg Cd/g of NZ. Isotherm curves at varying S/L ratios show a rapid increase without reaching a plateau. This is due to the increase of the zeolite mass with increasing S/L ratios and availability of more binding sites as the dosage of zeolite increases. Even though the isotherm curves show different behaviours, the highest value of q_e obtained at a single and at varying S/L ratios are similar, confirming that at saturated conditions the S/L ratio does not influence the amount of metal removed on zeolite. However, the value of q_e of IMZ is three-to-four times higher than to that of NZ. Evidently, the modification of natural zeolite has caused an increase in the quantity of metal ions removed, probably due to the increase of the net negative charge on the iron-modified zeolite surface, which is compensated by the presence of a higher amount of exchangeable cations, mostly sodium[21].

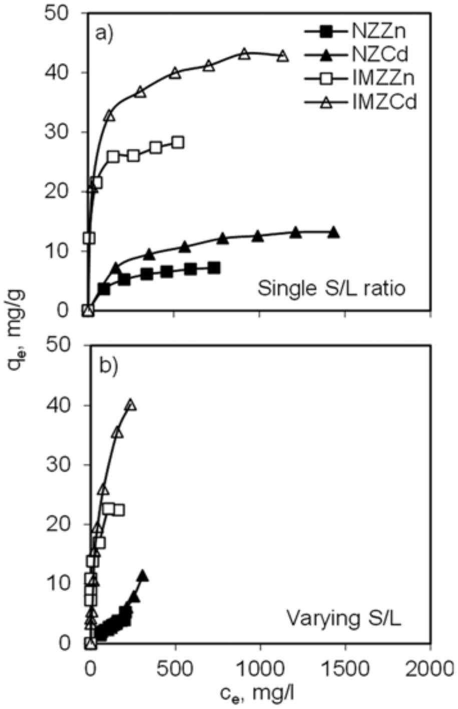

Fig. 2 — Sorption isotherms at: a) a single and b) varying S/L ratios.

This behaviour could be explained by analysing the results for exchangeable cations and *p*H values obtained at varying S/L ratios for NZ and IMZ. The concentrations of exchangeable (Na^+, K^+, Ca^{2+} and Mg^{2+}) cations which are leaving the zeolite structure and the concentrations of zinc and cadmium ions entering the zeolite structure at varying S/L ratios are shown in Figure 3.

For NZ an almost stoichiometric ratio between the amount of bound zinc and cadmium and released exchangeable cations is observed at all S/L ratios, while for IMZ, the stoichiometric ratio is evident only for the S/L ratio <10 g/L. For S/L>10 g/L the constant amount of removed metal ions is achieved (because the removal efficiency is almost 100%), while the amount of exchangeable cations increases. Among them, sodium dominates as the result of the modification of natural zeolite (Table 1). The consequence of the increase of their concentration in the solution is the increase of *p*H caused by the exchange of H^+ with exchangeable cations.

The results of $p\mathrm{H}_e$ of the suspensions in equilibrium for both metal cations and zeolite samples at varying S/L ratios (results not presented here) shows that for both metal cations, the equilibrium $p\mathrm{H}_e$ does not significantly change for NZ and it is around $p\mathrm{H}_e \approx 6$. For IMZ, the gradually increase of $p\mathrm{H}_e$ with the increasing S/L ratio is recorded for zinc up to $p\mathrm{H}_e=7.31$ while for cadmium up to $p\mathrm{H}_e=9.71$. At highest S/L ratios (for S/L>60 g/L) almost all Cd was removed onto IMZ. Thus, the increase of *p*H was due to the exchange of H^+ with exchangeable cations from IMZ according to the following reaction[21]:

$$\text{M-(IMZ)} + (\mathrm{H_2O})_x \rightleftarrows \text{H-(IMZ)} + (\mathrm{H_2O})_{x-n} + \mathrm{M}^{n+} + n\mathrm{OH}^- \quad \text{...(3)}$$

where:

M^{n+} - Na^+, K^+, Ca^{2+}, Mg^{2+}

IMZ - iron-modified zeolite.

The obtained results show the selection of the S/L ratio to be one of the critical parameters that must be considered in the implementation process in practice, especially with the IMZ sample. Even though a higher mass of IMZ ensures higher removal efficiency, it also causes an increase of *p*H in the suspension which can lead to the precipitation of metal ions.

Batch scale design

Two different design approaches were applied for batch scale design: the operating line method and the Rayleigh's method of dimensional analysis. The operating line method approach required the testing of experimental data according to the adsorption isotherm.

Testing of the adsorption isotherm

The sorption equilibrium is often described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent[23]. In order to optimize and effectively design the sorption system, it is important to determine the most appropriate correlation between the equilibrium results. In this study, Langmuir, Freundlich and Dubinin-Radushkevich isotherms given by equations (4)-(6) were used to fit the equilibrium data obtained at a single S/L ratio using the nonlinear regression analysis.

The Langmuir isotherm model describes monolayer sorption onto a homogenous surface and is given by equation[24-26]:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \qquad \text{...(4)}$$

where q_m is the maximum sorption capacity (mg/g) and K_L is the Langmuir constant related to the energy of sorption (l/mg).

The Freundlich isotherm assumes multilayer sorption on a heterogeneous surface and is given by equation[26,27]:

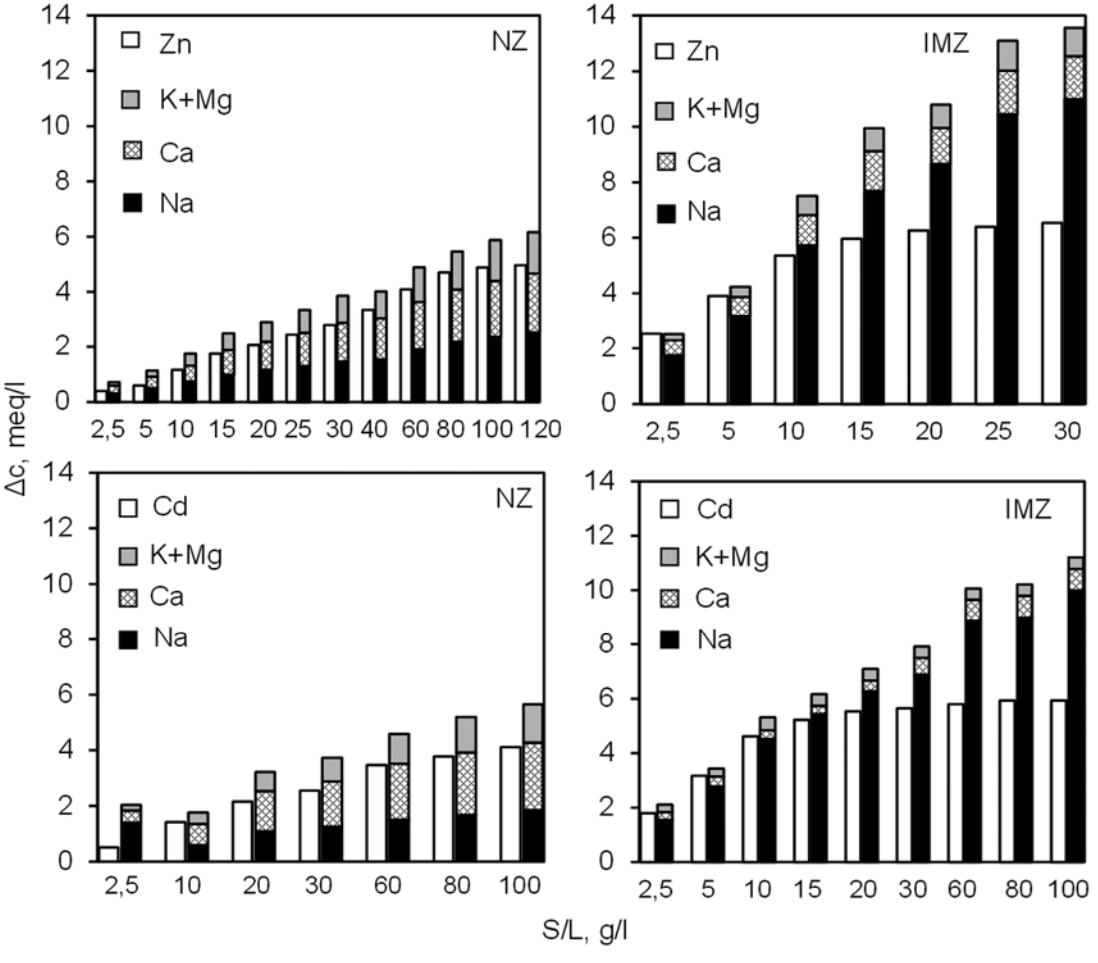

Fig. 3 — The relation between leaving and entering ions in equilibrium at varying S/L ratios.

$$q_e = K_F c_e^{1/n} \qquad ...(5)$$

where K_F is a constant indicative of the relative sorption capacity ($mg^{1-(1/n)} l^{1/n}/g$) and n is a constant indicative of the intensity of sorption.

The Dubinin-Radushkevich isotherm is applied to find out the sorption mechanism based on the potential theory assuming a heterogeneous surface. Equation is given[26-30]:

$$q_e = q_m e^{\left(\frac{(RT\ln(1+1/c_e))^2}{-2E^2}\right)} \qquad ...(6)$$

where E is the mean free sorption energy (kJ/mol), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

The calculated parameters of isotherms and correlation coefficients are compared and listed in Table 2. Figure 4 shows the experimental data and predicted isotherms using the nonlinear regression analysis.

For both metal cations, the Langmuir constant, K_L was significantly higher for the modified zeolite in comparison with natural zeolite. Higher values of K_L for IMZ indicate its greater affinity towards metal ions compared to NZ which is in agreement with the

Table 2 — Comparison of sorption isotherm parameters.

	Zn		Cd	
	NZ	IMZ	NZ	IMZ
	q_{exp}=7.190	q_{exp}=28.282	q_{exp}=13.239	q_{exp}=42.876
Langmuir				
q_m	8.271	27.397	14.599	42.194
K_L	0.008	0.106	0.006	0.038
R_L	0.246	0.028	0.201	0.041
r^2	0.989	0.992	0.986	0.985
Freundlich				
q_{mF}	7.770	32.775	14.241	48.355
K_F	0.858	9.032	1.709	12.100
n_F	3.039	5.195	3.470	5.311
r^2	0.974	0.928	0.982	0.954
Dubinin-Radushkevich				
q_m	7.126	28.501	13.394	42.011
E	1.155	4.472	1.199	3.585
r^2	0.987	0.988	0.992	0.989

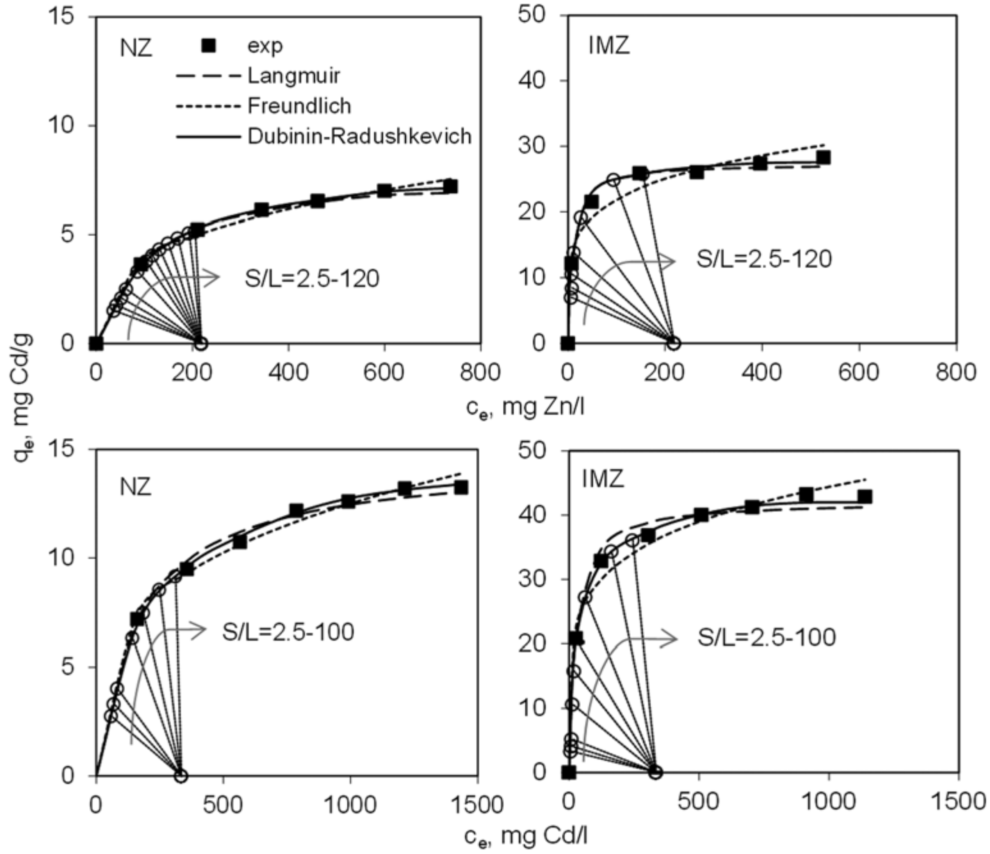

Fig. 4 — Experimental data obtained at a single S/L ratio, Langmuir, Freundlich and Dubinin-Raduskevich isotherms for zinc and cadmium uptake onto natural and iron-modified zeolite. Operating lines generated for the same initial concentration (c_o=217.37 mg Zn/L and c_o=333.63 mg Cd/L for NZ and IMZ) and different slope, V/m (varying S/L ratios).

experimentally determined capacity[31]. The value of K_L is related to the dimensionless constant separation factor, R_L which is given by following equation[26]:

$$R_L = \frac{1}{1 + K_L \cdot c_o} \quad ...(7)$$

The calculated values of R_L for all zeolites samples range from 0 to 1 indicating that the binding of zinc and cadmium on zeolite samples is the favoured sorption process. In spite of the higher value of the correlation coefficient, r^2, the value for capacity calculated from the model is different from the one experimentally determined, indicating the Langmuir isotherm inappropriate for the description of the experimental results.

The Freundlich isotherm equation fits well the experimental results based on the values of correlation coefficients, r^2. The values of constants, n for both metal cations are ≈3 for NZ and ≈ 5 for IMZ. It is generally stated that values of n in the range 2-10 represent the favoured sorption process, in the range 1-2 moderately and less than 1 poor sorption process[32,33]. This isotherm does not predict any saturation of zeolite by metal ions. To determine the maximum sorption capacity, it is necessary to operate with the constant initial concentration and different weights of sorbent. Thus ln q_{mF} is the extrapolated value of ln q_e for $c=c_o$ according to equation[32]:

$$K_F = \frac{q_{mF}}{c_o^{1/n}} \quad ...(8)$$

where q_{mF} is the Freundlich maximum sorption capacity (mg/g).

For the highest value of initial concentration, the q_{mF} value according to Eq. (8) was calculated. The calculated values for the maximum sorption capacity presented in Table 2 are higher compared to other isotherms indicating that this isotherm is not suitable for description of the experimental data.

The Dubinin-Radushkevich isotherm indicates good correlation with the experimental results according to the correlation coefficient. The calculated values for the medium sorption free energy, E (Table 2) provide information on the nature of the sorption process. The values are positive and lower than 8 kJ/mol. This indicates that the sorption process is endothermic and that physical sorption plays a significant role in the overall sorption process[34]. For both metal cations and zeolites samples, the values for calculated capacity are closer to experimentally determined capacity than with other isotherms, indicating that this model is the most appropriate among others to describe the experimental results.

For both metal cations and zeolite samples, the results for the correlation coefficient, r^2 as the indicator of the fitting between the experimental and predicted data values were generally high, $r^2>0.93$. However, when comparing the value for the calculated and experimentally determined capacity, the Dubinin-Raduskevich isotherm best describes the equilibrium data.

Batch scale design by applying the operating line method

According to the operating line method, the mass balance equation in a single stage batch reactor at equilibrium is given as[35]:

$$V(c_o - c_t) = m(q_t - q_o) \quad ...(9)$$

At equilibrium, this becomes:

$$V(c_o - c_e) = m(q_e - q_o) \quad ...(10)$$

For fresh mixed sorbent, q_o=0, equation (10) can be expressed as follows:

$$q_e = -\frac{V}{m}c_e + \frac{V}{m}c_o \quad ...(11)$$

Eq (11) represents the general form of the operating line.

The equilibrium sorption capacity for any initial metal concentration can be obtained from the operation line and isotherm best fits the experimental results. Among tested isotherms the best fits are obtained with the Dubinin-Raduskevich isotherm. The experimental data and the predicted Dubinin-Raduskevich isotherm obtained at a single S/L ratio are shown in Fig. 4, as well as a series of operating lines with a different slope for the solution volume/mass of zeolite, V/m (varying S/L ratio) and the same initial concentration (c_o=217.37 mg Zn/l and c_o=333.63 mg C/l for NZ and IMZ).

The equilibrium concentration for varying S/L ratios is predicted from the point of intersection of the operating line on the Dubinin-Raduskevich isotherm (from the data) obtained at a single S/L ratio and by using Eq (11). Figure 5 shows the predicted amount of metal uptake on zeolites, q_p for the same initial concentration and different slopes of V/m (varying S/L ratios) and the experimental data, q_{exp} obtained at the same condition.

The q_p values for sorption of zinc and cadmium onto NZ and IMZ at varying S/L ratios obtained from results at a single S/L ratio by using the operating line

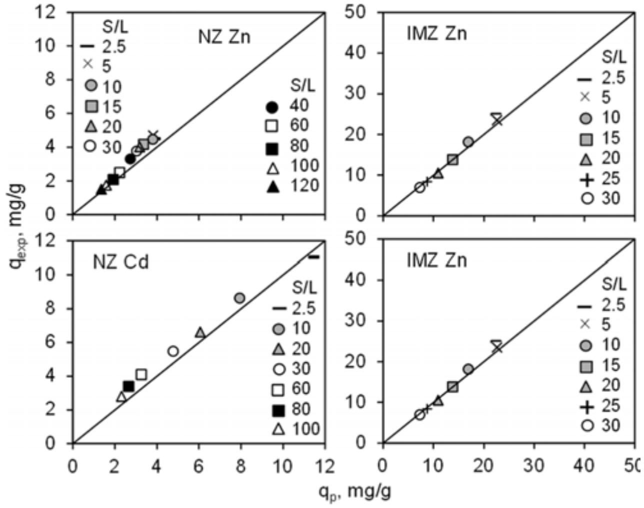

Fig. 5 — Comparison of the experimental, q_{exp} and predicted, q_p data for sorption of zinc and cadmium ions on NZ and IMZ at varying S/L ratios.

method are in reasonable agreement with the q_{exp} values obtained at the same condition. This indicates that based on one conducted experiment, at a single S/L ratio, by using the operating line method one can predict the amount of bound zinc and cadmium at varying S/L ratios.

In order to evaluate the fit of predicted and experimental data, apart from the correlation coefficient, r^2 the error functions are also calculated as follows[36,37] and listed in Table 3.

The sum of the squares of the errors (SSE):

$$SSE = \sum_{i=1}^{n} \left(q_p - q_{\exp} \right)^2 \qquad ...(12)$$

The sums of the absolute errors (SAE):

$$SAE = \sum_{i=1}^{n} \left| \left(q_p - q_{\exp} \right) \right| \qquad ...(13)$$

The average relative error (ARE):

$$ARE = \frac{\sum_{i=1}^{n} \left| \left(q_p - q_{\exp} / q_{\exp} \right) \right|}{n} \qquad ...(14)$$

The average relative standard error (ARS):

$$ARS = \sqrt{\frac{\sum_{i=1}^{n} \left[\left(q_p - q_{\exp} \right) / q_{\exp} \right]^2}{n-1}} \qquad ...(15)$$

where q_p is the predicted (calculated) data, q_{exp} is the experimentally obtained data and n is the number of experimental data points.

Table 3 — Error analysis by using the predicted, q_p value obtained from the Dubinin-Raduskevich isotherm parameters at a single S/L ratio and the experimental, q_{exp} data.

Samples	r^2	SSE	SAE	ARE	ARS
NZ Zn	0.991	3.557	5.211	0.186	0.208
IMZ Zn	0.994	2.642	3.109	0.048	0.058
NZ Cd	0.980	4.913	5.037	0.207	0.218
IMZ Cd	0.997	3.510	5.068	0.027	0.031

The results indicate a good agreement between predicted, q_p and experimental, q_{exp} values according to the correlation coefficient, r^2>0.98. From Table 3 the values of ARE and ARS (relative error) are smaller than the values of SSE and SAE (absolute error). The small values of the error function indicate better fitting and similarity of predicted and experimental data which is confirmed by Fig. 5.

Eq. (11) can be rearranged as follow[38]:

$$\frac{m}{V} = \frac{c_o - c_e}{q_e} \qquad ...(16)$$

The Dubinin-Raduskevich isotherm equation, Eq. (6) was substituted with q_e in Eq. (16) as follows:

$$\frac{m}{V} = \frac{c_o - c_e}{q_m e^{\left(\frac{RT \ln(1+1/c_e)^2}{-2E^2} \right)}} \qquad ...(17)$$

Eq (17) allows for calculation of the mass of zeolite needed for a given volume of metal solution, initial concentration and removal efficiency. Figure 6 shows a series of plots of 60-100% removal efficiency derived from Eq (17) with the initial concentration of 217.37 mg Zn/l and 333.63 mg Cd/l and different solution volumes.

The design objective is to reduce the metal solution concentration for the given volume of wastewater by using the minimal amount of zeolite in order to obtain the desired sorption efficiency. From Fig. 6, it is evident that for the same removal efficiency, a higher amount of NZ is required than of IMZ. Thus for the total removal efficiency, a 4.5 times higher amount of NZ is required for treatment of the same volume of zinc ions, for cadmium ions a 3.2 times higher amount of NZ is required compared to IMZ. That means that the complete removal of zinc from a 217.37 mg/L solution will take 345 g of NZ and 77 g of IMZ, and that of cadmium from 333.67 mg/L will take 271 g of NZ and 83 g of IMZ for the volume of 10 l. Recalculated as the S/L ratio, a complete removal of zinc ions will be achieved at S/L=34.5 g/l onto NZ

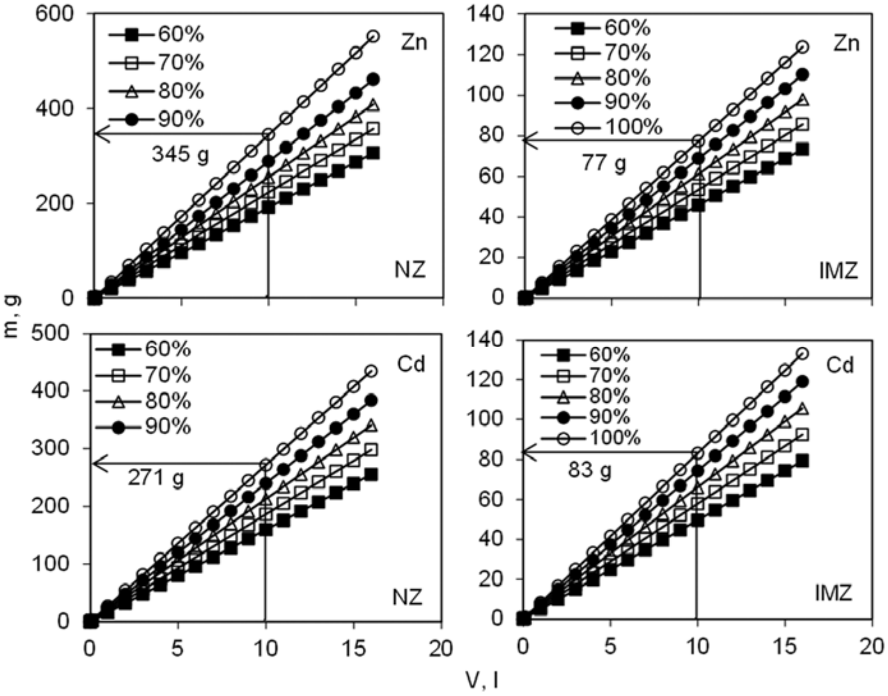

Fig. 6 — Zeolite mass *vs*. volume of metal solution for different sorption efficiencies (c_o=217.37 mg Zn/L and c_o=333.63 mg Cd/L for NZ and IMZ).

and S/L=7.7 g/L onto IMZ, and for cadmium ions at S/L=27.1 g/L onto NZ and S/L=8.3 g/L onto IMZ.

Batch scale design by applying the Rayleigh's method of dimensional analysis

The Rayleigh's method of dimensional analysis has also been used for the batch scale reactor design. This analysis is based on the assumption that the amount of metal removed on zeolite (m_e) is a function of the equilibrium concentration (c_e), solution volume (V) and zeolite amount (m). The functional dependence is given by equation[15]:

$$m_e = f(c_e, V, m) \qquad ...(18)$$

As only units for length (L) and mass (M) can be taken as fundamental units of measurement, the dimensions of the parameters will be:

$$[m_e] = \mathrm{M} \quad [c_e] = \mathrm{M/L^3} \quad [V] = \mathrm{L^3}, \text{ and } [m] = \mathrm{M} \qquad ...(19)$$

The ratio of $\dfrac{m_e/m}{c_e \cdot V/m}$ is a dimensionless quantity.

It is a function of c_e, V and m, from which a dimensionless combination cannot be formed. Therefore, we can express the equation as follows:

$$m_e/m = f\ (c_e \cdot V/m) \qquad ...(20)$$

and convert the Freundlich isotherm into the Power-function model (Freundlich-like):

$$m_e/m = K_{PF} \cdot (c_e \cdot V/m)^{n_{PF}} \qquad ...(21)$$

where K_{PF} and n_{PF} are empirical constants.

By dividing the amount of metal removed on zeolite (m_e) by the zeolite mass (m), the equilibrium amounts of metal uptake per gram of zeolite (q_e) can be obtained, and equation (21) is modified to:

$$q_e = K_{PF} \cdot (c_e \cdot V/m)^{n_{PF}} \qquad ...(22)$$

The logarithm form of the Power-function model is given by equation:

$$\log q_e = \log K_{PF} + n_{PF} \log(c_e \cdot V/m) \qquad ...(23)$$

This equation is applied to values of q_e and c_e for the experimental data obtained at varying S/L ratios (S/L=2.5-120 g/L for Zn and S/L=2.5-100 g/L for Cd) and constant initial concentrations of 217.37 mg Zn/l and 333.63 mg Cd/l. The parameters of Power-function models, n_{PF} and K_{PF} are calculated and listed in Table 4. The results show excellent fitting of experimental data with the Power-function model which is confirmed by high values of r^2.

In order to confirm the validity of dimensional analysis, Power-function parameters obtained at

Table 4 — Parameters of the Power-function model for zinc and cadmium sorption on zeolite samples.

Sample	Zn			Cd		
	K_{PF}	n_{PF}	r^2	K_{PF}	n_{PF}	r^2
Varying S/L ratios						
	S/L = 2.5-120 g/l; c_o = 218 mg Zn/l			S/L = 2.5-100 g/l; c_o = 334 mg Cd/l		
NZ	1.889	0.323	0.985	2.667	0.317	0.981
IMZ	12.947	0.203	0.963	15.827	0.220	0.980

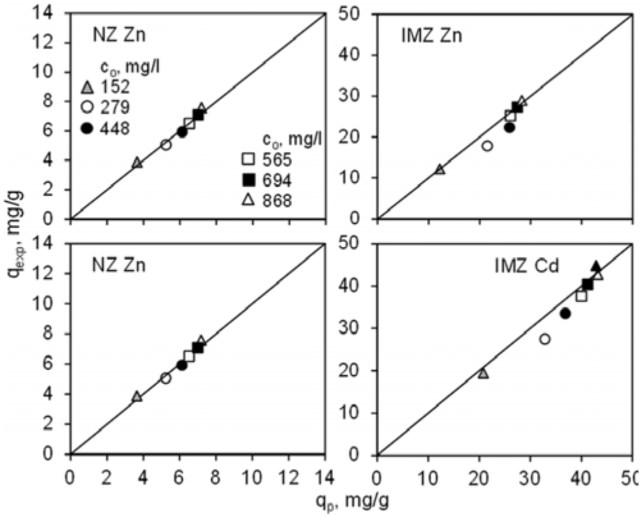

Fig. 7 — Comparison of the experimental, q_{exp} and predicted, q_p data for the sorption of zinc and cadmium ions on NZ and IMZ at a single S/L ratio (S/L=10) by using Power-function model parameters obtained at varying S/L ratios.

varying S/L ratios have been used to predict the amount of sorbed zinc and cadmium on NZ and IMZ at a single S/L ratio. The obtained parameters have been introduced into Eq. (22) as follows:

NZZn: $$q_e = 1.889 \cdot (c_e \cdot V / m)^{0.323} \quad \text{...(24)}$$

IMZZn: $$q_e = 12.947 \cdot (c_e \cdot V / m)^{0.203} \quad \text{...(25)}$$

NZZn: $$q_e = 2.667 \cdot (c_e \cdot V / m)^{0.317} \quad \text{...(26)}$$

NZZn: $$q_e = 15.827 \cdot (c_e \cdot V / m)^{0.220} \quad \text{...(27)}$$

For the given S/L ratio and desired residual concentration of metal ions the value of q_e could be predicted by means of equations (24)-(27).

The validity of these equations has been tested for the same experimental condition obtained in the experiment with a single S/L ratio in order to compare it with experimentally obtained results, which is shown in Fig. 7. Also, predicted, q_p and experimentally obtained, q_{exp} values have been compared with each other by the correlation coefficient and error analysis (SSE, SAE, ARE and ARS) in Table 5.

Table 5 — Error analysis by using predicted, q_p values obtained from Power-function model parameters at varying S/L ratios and experimental, q_{exp} data.

Samples	r^2	SSE	SAE	ARE	ARS
NZ Zn	0.972	0.282	1.098	0.033	0.043
IMZ Zn	0.933	26.827	8.797	0.061	0.099
NZ Cd	0.974	8.015	7.095	0.093	0.107
IMZ Cd	0.944	51.706	15.701	0.065	0.086

The predicted values, q_p are in good agreement with experimental, q_{exp} values obtained at the same conditions. This is supported by acceptable values of r^2 and low values of the error function. This indicates that on the basis of one conducted experiment, one can easily estimate the amount of bound zinc and cadmium on NZ and IMZ independently of the S/L ratio.

However, in this paper batch scale design was performed from a single solution in a single stage reactor. Thus, further investigation should be focused on designing a batch reactor with multi component solutions and in a two-stage reactor which is known to be more efficient in practical application.

Conclusion

The removal of zinc and cadmium on natural and iron-modified zeolite at varying S/L ratios and a constant initial concentration, as well as at a single ratio and different initial concentrations has been examined. The removal efficiency of zinc and cadmium increases, while the amount removed per gram of zeolite decreases with the increasing S/L ratio, due to availability of more binding sites as the dosage of zeolite increases. The maximum value of q_e is obtained for both zeolite samples and metal cations at S/L <5 g/L. The removal ability of IMZ towards zinc and cadmium is three to four times higher compared to NZ independently of experimental conditions. Also, for both metal cations, with the increasing S/L ratio, the equilibrium $p\text{H}_e$ value has not changed significantly for NZ, but did increase for

IMZ. Therefore, it is very important to choose an optimum S/L ratio in order to avoid the precipitation of metal ions, with the achievement of the maximum removal efficiency with the lowest zeolite mass.

Considering all applied isotherm models, the Dubinin-Raduskevich isotherm provides the best correlation. Batch scale design is focused on prediction on the amount removed per gram of zeo lite at a single and at varying S/L ratios. Two methods were applied and compared in the batch scale design, the operating line method with the Dubinin-Raduskevich isotherm and the Rayleigh's method of dimensional analysis. Both methods are efficient in prediction of the amount of removed zinc and cadmium ions per gram of natural and iron-modified zeo lite from single solution independently of the S/L ratio.

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References

1 Nagajyoti P C, Lee K D & Sreekanth T V M, *Environ Chem Lett,* 8 (2010) 199.

2 Alloway B J & Ayres D C, *Chemical principles of environmental pollution*, (Blackie Academic & Professional, Chapman & Hall, London), 1993.

3 Barakat M A, *Arabian J Chem,* 4 (2011) 361.

4 Fenglian F & Qi W, *J Environ Manage,* 92 (2011) 407.

5 Volesky B, *Hydrometallurgy,* 59 (2001) 203.

6 Bosso S T & Enzweiler J, *Water Res,* 36 (2002) 4795.

7 Kragović M, Daković A, Sekulić Ž, Trgo M, Ugrina M, Perić J & Gatta G D, *Appl Surf Sci,* 258 (2012) 3667.

8 Minceva M, Fajgar R, Markovska L & Meshko V, *Sep Sci Technol,* 43 (2008) 2117.

9 Misaelides P, *Micropor Mesopor Mater,* 144 (2011) 15.

10 Wang S & Peng Y, *Chem Eng J,* 156 (2010) 11.

11 Kumar K V & Pordoki K, *Dyes Pigm,* 74 (2007) 590.

12 Puls R W, Powell R M, Clark D & Eldred C J, *Water Air Soil Poll,* 57 (1991) 423.

13 Utomo H D & Hunter K A, *Biores Technol,* 101 (2010) 1482.

14 Zhao L X & Hou W G, *Colloid Surface A,* 396 (2012) 29.

15 Chang T W & Wang M K, *Chemosfere,* 48 (2002) 419.

16 Kosmulski M, *Colloid Surface A,* 149 (1999) 397.

17 Shrotri S, Harris C C, Huang L & Somasundaran P, *Colloid Surface A,* 141 (1998) 189.

18 Zhao L X, Song S E, Du N & Hou W G, *Acta Phys Chim Sin,* 28 (2012) 2905.

19 DiToro D M, Mahony J D, Kirchgraber P R, O´Byrne A L, Pasquale L R & Piccirilli D C, *Environ Sci Technol,* 20 (1986) 55.

20 Voice T C & Weber W J, *Environ Sci Technol*, 19 (1985) 789.

21 Ugrina M, Vukojević Medvidovć N & Daković A, *Desalin Water Treat*, 53 (2015) 3569.

22 Abd El-Latif M M, Ibrahim A M & El-Kady M F, *J Am Sci,* 6 (2010) 267.

23 Ho Y S, Porter J F & McKay G, *Water Air Soil Poll,* 141 (2002) 1.

24 Langmuir I, *J Am Chem Soc,* 40 (1918) 1361.

25 Langmuir I, *J Am Chem Soc,* 38 (1916) 2221.

26 Foo K Y, Hameed B H, *Chem Eng J,* 156 (2010) 2.

27 Freundlich H M F, *Z Phys Chem,* 57 (1906) 385.

28 Dubinin M M, *Zh Fiz Khim,* 39 (1965) 1305.

29 Radushkevich L V, *Zh Fiz Khim*, 23 (1949) 1410.

30 Günay A, Arslankaya E & Tosun İ, *J Hazard Mater,* 146 (2007) 362.

31 Vijayaraghavan K, Padmesh T V N, Palanivelu K & Velan, *J Hazard Mater,* 33 (2006) 304.

32 Hamdaoui O & Naffrechoux E, *J Hazard Mater,* 14 (2007) 381.

33 Vargas A M M, Cazetta A L, Kunita M H, Silva T L & Almeida V C, *Chem Eng J,* 168 (2011) 722.

34 Saltali K, Sari A & Aydin M, *J Hazard Mater,* 141 (2007) 258.

35 Ho Y S, *Adsorption,* 7 (2001) 139.

36 Hossain M A, Ngo H H, Guo W S & Nguyen T V, *Bioresource Technol,* 113 (2012) 97.

37 Han R, Zhang J, Han P, Wang Y, Zhao Z & Tang M, *Chem Eng J*, 145 (2009) 496.

38 Khalid Mahmoud D, Amran Mohd Salleh M & Wan Abdul Karim W A, *J Purity Utility Reaction Environ*, 2 (2013) 14.