

## Optimization of parameters for competitive adsorption of heavy metal ions ( $\text{Pb}^{+2}$ , $\text{Ni}^{+2}$ , $\text{Cd}^{+2}$ ) onto activated carbon

Mohammad Kavand, Tahereh Kaghazchi, and Mansoor Soleimani<sup>\*</sup>

Department of Chemical Engineering, AmirKabir University of Technology,  
No. 424, Hafez Ave., P. O. Box 15875-4413, Tehran, Iran  
(Received 9 July 2013 • accepted 16 December 2013)

**Abstract**—This study investigates optimization of various competitive adsorption parameters for removal of Cd(II), Ni(II) and Pb(II) from aqueous solutions by commercial activated carbon (AC) using the Taguchi method. Adsorption parameters such as initial metal concentration of each metal ion ( $C_{0,i}$ ), initial pH ( $\text{pH}_0$ ), adsorbent dosage ( $m$ ) and contact time ( $t$ ) in batch technique were studied to observe their effects on the total adsorption capacity of metals onto activated carbon ( $q_{\text{tot}}$ ). The adsorbent dosage has been found to be the most significant parameter. Interactions between  $C_{0,\text{Cd}} \times C_{0,\text{Ni}}$ ,  $C_{0,\text{Cd}} \times C_{0,\text{Pb}}$  and  $C_{0,\text{Ni}} \times C_{0,\text{Pb}}$  have been considered for simultaneous metal ions adsorption. The optimum condition for adsorption of metal ions were obtained with  $C_{0,i}=100 \text{ mg L}^{-1}$ ,  $\text{pH}_0=7$ ,  $m=2 \text{ g L}^{-1}$  and  $t=80 \text{ min}$ . Finally, experimental results showed that a multi-staged adsorptive treatment would be necessary to reach the minimal discharge standards of metal ions in the effluent.

Keywords: Heavy Metals, Competitive Adsorption, Activated Carbon, Multi-component

### INTRODUCTION

Environmental contamination with heavy metals is caused by several industries such as oil refinery plants, metal plating, mining, painting, and car radiator manufacturing, and also by agricultural sources such as fertilizers and fungicidal sprays. The presence of heavy metals in the environment is a major concern because of their toxicity and threat for human life and for the environment, especially when tolerance levels are exceeded [1]. In this context, the recovery of heavy metals from wastewater has become a major topic of research in water treatment. Cadmium (Cd(II)) is a non-essential and a non-biodegradable metal ion which slowly accumulates in the body of living creatures, usually through the food chain [2,3]. Nickel salts are commonly used in metal plating and its concentration in industrial wastewater varies between 6 to  $12 \text{ mg L}^{-1}$ , which is above the safe limit. The chronic toxicity of nickel to humans and the environment is well known and high nickel concentration causes gastrointestinal irritation and lung and bone cancers [4]. Lead is an important compound used as an intermediate in processing industries such as plating, paint and dyes, glass operations, and lead batteries. However, its presence in water even at a very low level would be harmful to aquatic life and human health due to its toxicological, potential carcinogenic and neurotoxic effects [5]. The tolerance limits for Cd(II), Pb(II) and Ni(II) ions in industrial effluent discharging into the inland surface waters are 2, 0.1 and  $3 \text{ mg L}^{-1}$ , respectively [6].

Several methods are commonly used for these metals adsorption such as chemical precipitation, membrane filtration and ion exchange, but adsorption has been shown to be an economical alter-

native for removing metal traces from water [7].

So far, the interest in adsorption of heavy metal ions onto activated carbon has been focused on adsorption of single component system. However, wastewater is a complicated mixture containing more than one metal ion. Recently, a number of studies were carried out on competitive adsorption of metal ions onto various adsorbents [8-13].

The investigation of adsorption behavior of activated carbons and natural adsorbents for recovery of heavy metals from single component solutions has been the aim of many previous studies [14-21]. In this study, the feasibility of activated carbon application for competitive adsorption of various heavy metal ions was evaluated. The main aim is maximizing the selected response characteristic (total adsorption of metal ions by activated carbon ( $q_{\text{tot}}$ )) by optimizing various parameters affecting the competitive adsorption of Cd(II), Ni(II) and Pb(II) metal ions from aqueous solutions. The effects of individual parameters and their interactions on  $q_{\text{tot}}$  will be examined using the Taguchi method.

### MATERIAL AND METHODS

#### 1. Adsorbent and Adsorbates

The commercially available granular activated carbon (16-50 mesh) was purchased from INDOGERMAN (wt -c830) and pre-conditioned prior to use in the experiments. Granulated activated carbon was washed with deionized water. Treated activated carbon was dried in an oven at  $105^\circ\text{C}$  and stored until use. The main characteristics of this carbon have been listed in Table 1.

Standard stock solutions of Ni(II), Cd(II) and Pb(II) ( $1,000 \text{ mg L}^{-1}$ ) were prepared by dissolving spectral pure grade chemicals  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  (MERCK, Germany) in deionized water, respectively. The stock solution for each metal salt was diluted with DW to obtain metal ion concentration in the range of 0-100 mg/l for use in the experiments. Atomic absorption spectro-

<sup>\*</sup>To whom correspondence should be addressed.

E-mail: soleimanim@aut.ac.ir, mansoreh\_soleimani@yahoo.com

Copyright by The Korean Institute of Chemical Engineers.

**Table 1. Characteristics of the activated carbon**

Specification	Values
Mesh size	16*50
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	913
Iodine number ( $\text{mg I}_2 \text{g}^{-1}$ )	950
Apparent density ( $\text{g mL}^{-1}$ )	0.48
Hardness no.	98
Moisture (%)	4
Ash (%)	3

photometer (VARIAN- AA240, Australia) was applied for metals analyzing at the wavelength of 228.8, 232 and 213.9 nm, for Cd(II), Ni(II) and Pb(II), respectively, by using air-acetylene flame.

## 2. Design of Experiments

We selected Taguchi's methodology for optimizing parameters in the simultaneous adsorption of Cd(II), Ni(II) and Pb(II) metal ions from aqueous solutions by activated carbon. The process parameters having significant impact on adsorption were selected (Table 2). To understand the interactive effects of initial concentration of metal ions, three interactive parameters were also studied. Accord-

**Table 2. Parameters for multi-component adsorption of metal ions onto AC**

Parameter	Units	1-Level	2-Level	3-Level
<b>A:</b> Initial concentration of nickel ( $\text{C}_0$ , Ni)	$\text{mg L}^{-1}$	0	50	100
<b>B:</b> Initial concentration of cadmium ( $\text{C}_0$ , Cd)	$\text{mg L}^{-1}$	0	50	100
<b>C:</b> Initial concentration of lead ( $\text{C}_0$ , Pb)	$\text{mg L}^{-1}$	0	50	100
<b>D:</b> Initial pH of solution ( $\text{pH}_0$ )	-	3	5	7
<b>E:</b> Adsorbent dose (m)	$\text{g L}^{-1}$	2	6	10
<b>F:</b> Contact time (t)	min	40	80	120

**Table 3. Column assignment for the various factors and three interactions in Taguchi's  $\text{L}_{27}$  orthogonal array and experimental  $q_{\text{av}}$  values**

Exp. no	1 A	2 B	3 A×B	4 A×B	5 C	6 A×C	7 A×C	8 B×C	9 D	10 E	11 B×C	12 F	$R_1^*$	$R_2^*$	$R_{\text{avg}}^*$	S/N
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	1	1	1	1	1	1	1	1	7.35	7.40	7.380	17.36
3	0	0	0	0	2	2	2	2	2	2	2	2	7.68	7.66	7.665	17.70
4	0	1	1	1	0	0	0	1	1	1	2	2	8.30	8.33	7.315	18.40
5	0	1	1	1	1	1	1	2	2	2	0	0	7.05	7.08	7.065	16.98
6	0	1	1	1	2	2	2	0	0	0	1	1	26.95	27.03	26.980	28.62
7	0	2	2	2	0	0	0	2	2	2	1	1	9.26	9.27	9.265	19.34
8	0	2	2	2	1	1	1	0	0	0	2	2	35.12	35.09	35.105	30.91
9	0	2	2	2	2	2	2	1	1	1	0	0	18.62	18.66	18.64	25.41
10	1	0	1	2	0	1	2	0	1	2	0	1	3.35	3.42	3.385	10.59
11	1	0	1	2	1	2	0	1	2	0	1	2	30.71	30.74	30.725	29.75
12	1	0	1	2	2	0	1	2	0	1	2	0	9.62	9.69	9.655	19.69
13	1	1	2	0	0	1	2	1	2	0	2	0	15.95	15.99	15.970	24.07
14	1	1	2	0	1	2	0	2	0	1	0	1	9.31	9.27	9.290	19.36
15	1	1	2	0	2	0	1	0	1	2	1	2	14.11	14.08	14.095	22.98
16	1	2	0	1	0	1	2	2	0	1	1	2	11.72	11.68	11.700	21.36
17	1	2	0	1	1	2	0	0	1	2	2	0	10.61	10.50	10.555	20.49
18	1	2	0	1	2	0	1	1	2	0	0	1	45.61	45.71	45.660	33.19
19	2	0	2	1	0	2	1	0	2	1	0	2	7.92	7.97	7.945	18.00
20	2	0	2	1	1	0	2	1	0	2	1	0	4.52	4.56	4.540	13.14
21	2	0	2	1	2	1	0	2	1	0	2	1	41.60	41.61	41.605	32.82
22	2	1	0	2	0	2	1	1	0	2	2	1	5.75	5.74	5.745	15.19
23	2	1	0	2	1	0	2	2	1	0	0	2	39.15	39.21	39.180	31.86
24	2	1	0	2	2	1	0	0	2	1	1	0	22.90	22.86	22.880	27.19
25	2	2	1	0	0	2	1	2	1	0	1	0	22.95	22.99	22.970	27.23
26	2	2	1	0	1	0	2	0	2	1	2	1	23.95	23.88	23.915	27.57
27	2	2	1	0	2	1	0	1	0	2	0	2	13.85	13.89	13.870	22.84

\* $R_1$  and  $R_2$  are responses (total capacity of metal ions adsorption ( $\text{mg g}^{-1}$ ))

$R_{\text{avg}}$ : average of  $R_1$  and  $R_2$

ing to this method,  $L_{27}$  orthogonal array (OA) was suitable to determine the effects of the factors and the optimum operating conditions, with six parameters, each at three levels and three second-order interactions. Table 3 shows the selected  $L_{27}$  OA with assignment of parameters and interactions. All experiments were carried out twice under the same conditions.

### 3. Batch Experimental Adsorption Studies

For each experimental run, 50 ml of the aqueous solution of known concentration of either Cd(II) or Ni(II) and Pb(II), was taken in 150 ml conical flask containing pre-weighed amount of AC. These flask were agitated at a constant shaking rate of 220 rpm in a temperature-controlled orbital shaker (N-Biotek Orbital Shaking Incubator, NB-205) maintained at 30 °C. The initial pH ( $pH_0$ ) of solution was adjusted using 1 N  $HNO_3$  or 1 N NaOH aqueous solution without any further adjustment during the sorption process. The metal concentration retained in the adsorbent phase was calculated by following equation:

$$q_e = (C_0 - C_e)/m \quad (1)$$

where  $C_0$  and  $C_e$  are initial and equilibrium concentrations ( $mg\ L^{-1}$ ) of metal ion solution respectively;  $V$  is the volume of solution (L); and  $m$  is the mass of the adsorbent (g). The adsorption of metal ions from the solution and the equilibrium adsorption uptake in the solid phase,  $q_{tot}$  ( $mg/g$ ), was calculated using the following relationship [22]:

$$q_{tot} = \sum_{k=1}^3 (C_{0,i} - C_{e,i})/m \quad (2)$$

The sorption percentage (% adsorption) of metal ions from aqueous solution is computed as follows:

$$\text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

### 4. Analysis of Experiments

The obtained experimental data was processed with the “higher is better” (HB) quality characteristic to determine the optimum conditions, identify individual parameters of significance and estimate total metal adsorption ( $q_{tot}$ ) at the optimum conditions [23]. The plot of average response curves, analysis (ANOVA) for raw data and signal-to-noise ratio (S/N) data were used for data analysis in Taguchi method. After determination of the optimum condition, the mean of the response ( $\mu$ ) at the optimum condition was predicted. The mean at the optimal condition (optimal value of the response characteristic) was estimated as [22,23]:

$$\mu = \bar{T} + (\bar{A}_2 - \bar{T}) + (\bar{B}_2 - \bar{T}) = \bar{A}_2 + \bar{B}_2 - \bar{T} \quad (4)$$

where  $\bar{T}$  is the overall mean of the response, and  $\bar{A}_2$  and  $\bar{B}_2$  represent average values of response at the second levels of parameters A and B, respectively.

The average results for each level of parameters are listed in Table 3. Taguchi defines the loss function  $L(y)$  as a quantity proportional to the deviation from the nominal quality characteristic. In the case of HB type quality characteristics, the loss function is given by the following equation [24,25]:

$$L(y) = \frac{\frac{1}{y_1^2} + \frac{1}{y_2^2} + \frac{1}{y_3^2} + \dots}{n} \quad (5)$$

The S/N ratio consolidates several repetitions (at least two data points are required) into one value. The equation for calculating S/N ratios for HB-type characteristics is as follows [24,25]:

$$(S/N) = -10 \log \left( \frac{1}{n} \sum_{i=1}^R \frac{1}{y_i^2} \right) \quad (6)$$

where  $y_i$  is the value of the characteristic in an observation  $i$  and  $n$  is the number of observations or number of repetitions in a trial.

### 5. Kinetic Experiments

To study kinetic parameters in this adsorption system, batch tests were performed to determine kinetics parameters of adsorption. In these experiments, the effect of contact time on the metals adsorption by AC from solutions with different initial concentrations of metal ions of 50, 100 and 200  $mg\ L^{-1}$  has been investigated. The other operating parameters were: carbon dosage: 4 g  $L^{-1}$ , contact time: 3–360 min, temperature: 25 °C, shaking rate: 220 rpm.

### 6. Desorption Experiments

In these tests, desorption studies were examined for reusability of activated carbon. The fresh AC was saturated with each of the metal ions, in the single and ternary systems, under the conditions as follows:

AC dosage: 5 g  $L^{-1}$ , initial pH: 7.0, and shaking time: 3 h.

Subsequently, the metal-loaded AC was filtered and washed with distilled water sequentially several times to remove the residual unadsorbed metal ions. After drying, 0.25 g of the saturated sorbents was treated with 50 mL of extractant solutions including  $HNO_3$  and HCl (in various concentrations: 0.01, 0.1, 0.5 and 1 M) for 3 h. Desorption percentage was calculated from the amount of metal ions desorbed divided by the amount of metal ions adsorbed.

## RESULTS AND DISCUSSION

### 1. Effect of Process Parameters

The observed results for the effect of process parameters are illustrated in Fig. 1. In this figure, values of  $q_{tot}$  increased as the initial concentration of the metal ions were increased. This result (Fig. 1(a), (b) & (c)) may be a result of high driving force for mass transfer [22,26]. Fig. 1 shows an increase in  $q_{tot}$  with increasing the contact time from 40 to 80 minutes. However,  $q_{tot}$  decreases with further increase in time from levels 80 to 120 min. The results revealed that adsorption of species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. Between these two stages of the adsorption, the rate of sorption is found to be nearly constant. This is obvious by the fact that a large number of vacant surface sites are available for sorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute ions on the solid and the bulk phases [26,27]. Thereafter, the metal ions have to travel further deep into the pores with much larger resistance [25].

These results indicated a decrease in the rate of adsorption later on. Therefore, the adsorption of metal ions increases with time until equilibrium is reached between the solute molecules in the liquid and the solid phases [25–27].

An increase in  $pH_0$  showed higher adsorption capacity up to 7. Because of having functional groups on AC surface, these groups can have the potential for forming chelates easily with the metal

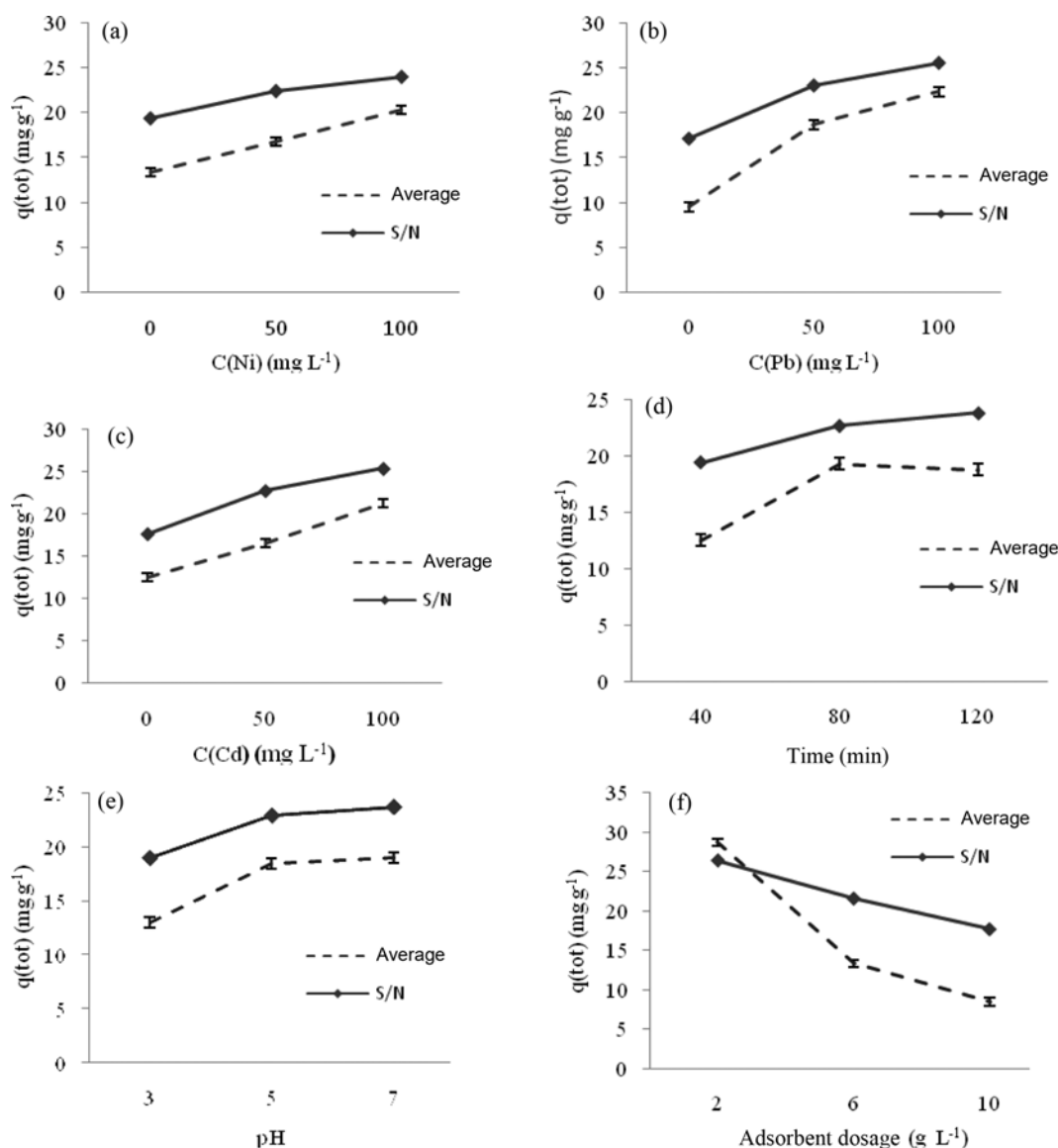
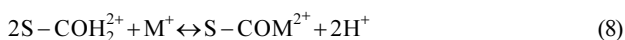
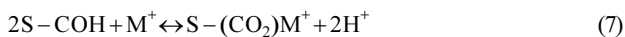


Fig. 1. Effect of process parameters on  $q_{\text{tot}}$  for multi component adsorption of metal ions onto AC (a)  $C_{0,\text{Ni}}$ ; (b)  $C_{0,\text{Pb}}$ ; (c)  $C_{0,\text{Cd}}$ ; (d) contact time; (e)  $\text{pH}_0$  and (f) adsorbent dosage.

ions and improve the activated carbon surface. Consequently, such negatively charged groups were showing affinity towards the positively charged or neutral metal species due to electrostatic interaction. These interactions may be responsible for the significant adsorption of metal ions by the following possible reactions [1,29]:



where M=Metal species of Pb, Ni or Cd

S=activated carbon surface

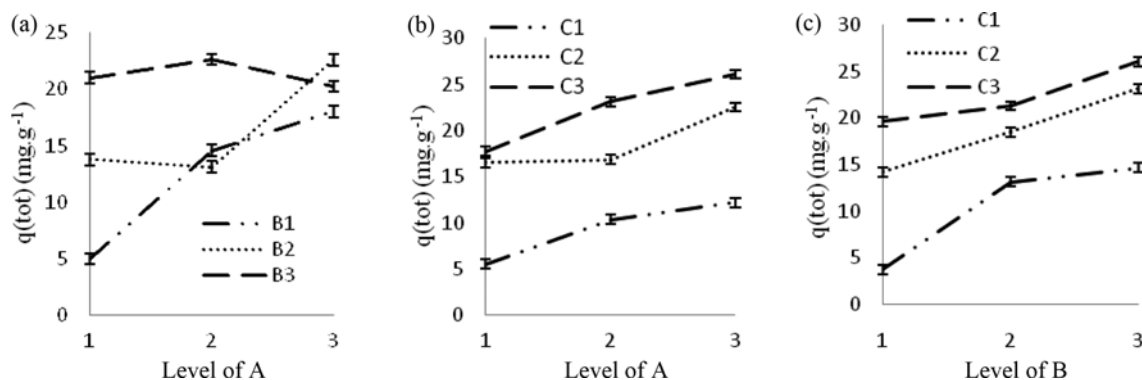
The above mechanism has been confirmed by an increasing initial metal ion concentration in aqueous solution as the final pH of solution decreases. This clearly indicates that sorption of more metal ions releases more  $\text{H}^+$ .

At lower pH values (<3.0), the active sites of the adsorbent are less available for metal ions due to protonation of the active sites at

higher  $\text{H}^+$  concentration. At moderate pH values (e.g. 3.0-6.0), linked  $\text{H}^+$  is released from the active sites and adsorbed amount of the metal ions is increased. In this pH range, it is believed that the ion exchange and complex formation processes are the major mechanisms for adsorption of single metal ions from solution. At pH the values higher than 6.0, both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal adsorption process. For this reason, the optimum pH value for adsorption of multi component system is 7 [1,28-29].

As adsorbent dosage (m) increased from 2 to 10 g L<sup>-1</sup>, the values of  $q_{\text{tot}}$  decreased. This is attributed to the decrease in unit adsorption as m increased, even though the adsorption of metal ions increased due to availability of larger surface area and more adsorption sites [25].

The interaction between initial concentrations of Cd(II), Ni(II) and Pb(II) metal ions affects the average value of  $q_{\text{tot}}$ . Fig. 2 shows that interactions at lower concentrations are more pronounced for



**Fig. 2.** The interaction between parameters (A, B, C) at three levels on  $q_{tot}$  for multi-component adsorption of metal ions. (a) interaction between A×B ( $C_{0, Ni}$  &  $C_{0, Cd}$ ), (b) interaction between A×C ( $C_{0, Ni}$  &  $C_{0, Pb}$ ), (c) interaction between B×C ( $C_{0, Cd}$  &  $C_{0, Pb}$ ).

all possible interactions, because there is competition between the different metal ions to occupy vacant adsorption sites on the surface [25]. As can be seen in Fig. 2 the interaction between A×B ( $C_{0, Ni}$  &  $C_{0, Cd}$ ) is effective more than other interactions, that is according to the result of ANOVA in Table 4.

In the analysis of variance (ANOVA), many quantities such as degrees of freedom and sum of squares are computed and organized in a standard tabular format. ANOVA results for raw and S/N ratio data with  $q_{tot}$  are given in Tables 4 and 5. Based on these results, it has been found that parameters  $C_{0, is}$ , pH<sub>0s</sub>, adsorbent dosage and contact time significantly affect the  $q_{tot}$  values. Also, the inter-

action effect of concentration of one metal ion with respect to other metal ion has significant influence on  $q_{tot}$  values. Individually, level 1 of adsorbent dosage (E), level 3 of pH<sub>0</sub> (D) and level 3 of  $C_{0, Pb}$  (C) have the highest influence on  $q_{tot}$ .

The F-ratio was used to determine which parameters have a significant effect on the performance characteristic [30]. The calculated values are compared with F values predicted by statistical F distribution (in Fischer tables) [30]. According to F-ratio values, importance of each factor in the different confidence can be investigated. From the Fisher tables with 90% and 95% confidence, the F values are

**Table 4.** ANOVA of  $q_{tot}$  raw ratio data for multi-component adsorption of metal ions onto AC

Parameter	DOF	Sum of squares	Variance	F-ratio (F)	% Contribution
A	2	430.247	215.123	150.131	5.201
B	2	691.253	345.626	241.207	8.377
C	2	1578.840	789.420	550.924	19.179
D	2	399.122	199.561	139.270	4.822
E	2	4014.060	2007.030	1400.680	48.816
F	2	511.327	255.663	178.423	6.187
A×B	4	459.197	229.608	80.117	5.518
A×C	4	50.389	25.194	8.791	0.581
B×C	4	40.917	20.458	7.139	0.427
Other/error	2	41.553	1.432		0.930
Total	26	8216.910			100

**Table 5.** ANOVA of S/N ratio data for multi-component adsorption of metal ions onto AC

Parameter	DOF	Sum of squares	Variance	F-ratio (F)	% Contribution
A	2	95.051	47.525	14.979	6.028
B	2	279.378	139.689	43.029	18.554
C	2	336.991	168.495	53.108	22.469
D	2	116.159	58.079	18.306	7.462
E	2	345.996	172.983	54.523	23.079
F	2	93.944	46.972	14.805	5.952
A×B	4	86.025	42.920	6.778	4.985
A×C	4	29.781	14.890	2.346	1.160
B×C	4	81.920	40.955	6.454	4.703
Other/error	2	6.345	3.172		5.610
Total	26	1471.560			100

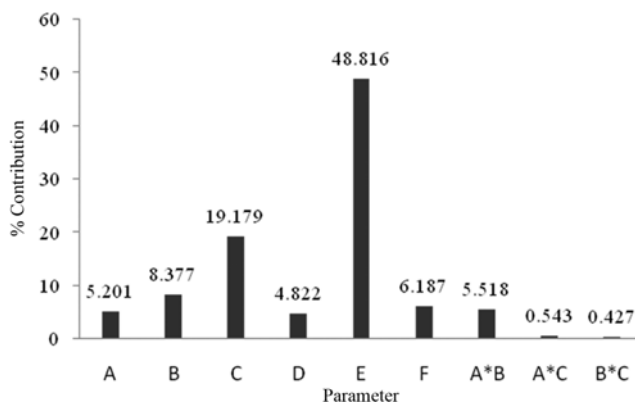


Fig. 3. Percent contribution of various parameters for  $q_{tot}$  for multi-component adsorption of metal ions onto AC: A,  $C_{0,Ni}$ ; B,  $C_{0,Cd}$ ; C,  $C_{0,Pb}$  ( $\text{mg L}^{-1}$ ); D,  $\text{pH}_0$ ; E,  $m$  ( $\text{g L}^{-1}$ ); and F,  $t$  (min).

- $F_{0.1,2,2}=9$ ,  $F_{0.05,2,2}=19$  for parameters
- and  $F_{0.1,4,2}=9.24$ ,  $F_{0.05,4,2}=19.2$  for interactions.

According to these values, all the parameters are found to be statistically significant at 90% and 95% confidence levels for raw data. Based on these results, in 95% degree of confidence only the interaction A×B between is important. The percentage of contribution of various parameters for raw data for multi-component adsorption of metal ions is shown in Fig. 3.

The above statement agrees with earlier reports [31,32]. Srivastava et al. studied sorption of  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  metal ions from aqueous solutions by bagasse fly ash [22,25]. They reported that adsorbent dosage is the most significant parameter with 47.38% con-

tribution to the  $q_{tot}$ . Yetilmezsoy et al. [33] reported that the effects of independent variables and optimum variables were 3.97 for initial pH of the solution, 43.4  $\text{mg L}^{-1}$  for initial concentration of  $\text{Pb(II)}$  ions, and 68.7 min for contact time with a predicted  $\text{Pb(II)}$  removal efficiency of about 100%. Özer et al. also investigated biosorption of copper ions using response surface methodology (RSM) [34]. The optimum biosorption conditions were determined as initial pH 4.0, temperature 25 °C, biosorbent concentration 1.2  $\text{g L}^{-1}$  and initial copper (II) concentration 200  $\text{mg L}^{-1}$ . The copper (II) biosorption attained equilibrium after 60 min and this contact time was taken as the equilibrium.

## 2. Contour Plots

Corresponding contour plots can facilitate the straightforward examination of the effects of the experimental variables on the responses. The relationship between the dependent and independent variables was further elucidated by constructing contour plots. Fig. 4 shows the corresponding contour plots as the functions of metal ions concentration, AC dosage, pH and contact time.

As it is seen from this figure, relatively steep curvatures in Pb, Cd and Ni concentrations curves indicated that the responses of adsorption were very sensitive to these parameters. Through these contour plots, it is also very easy and convenient to locate optimum levels of variables selection of optimal levels and estimation of optimum response characteristics.

The optimal level of various parameters was obtained after examining the response curves (Fig. 1) of the average value of  $q_{tot}$ . The first level of adsorbent dosage; the second level of contact time; and the third level of  $\text{pH}_0$  and initial concentrations ( $C_{0,i}$ ) have higher average values of  $q_{tot}$ . Thus, the significant process parameters affect

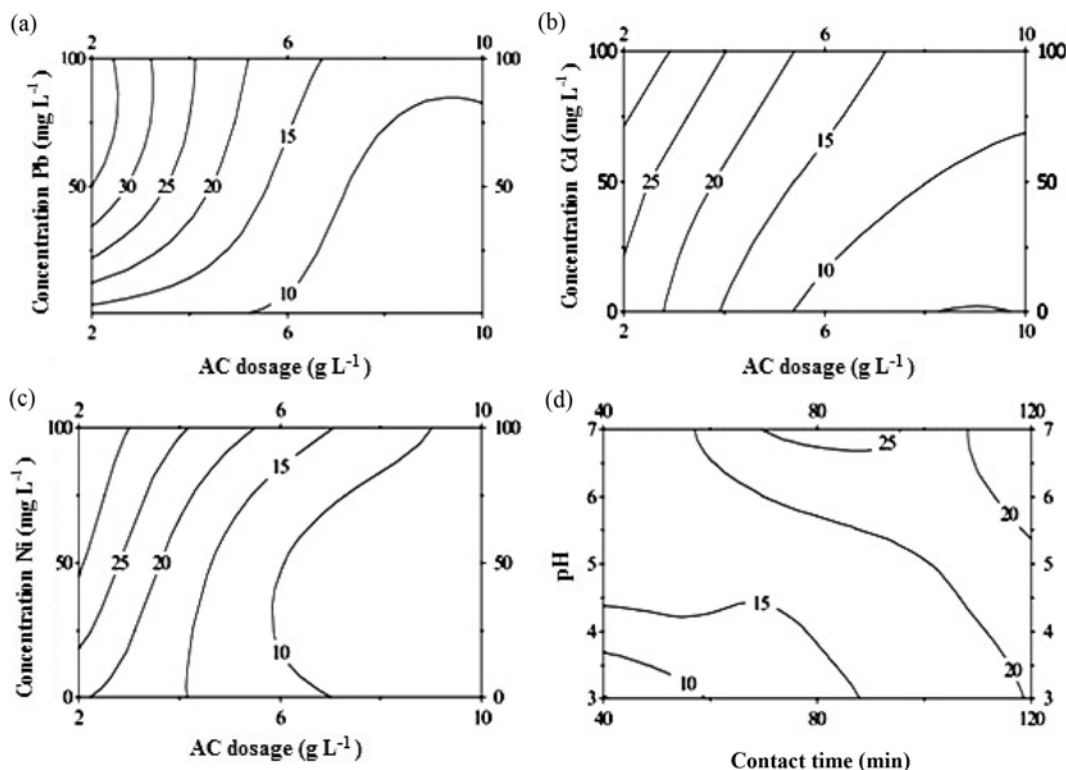


Fig. 4. Contour plots for  $q_{tot}$  as a function of process parameters: (a) Pb concentration and AC dosage; (b) Cd concentration and AC dosage; (c) Ni concentration and AC dosage and (d) pH and contact time.

**Table 6. Pseudo first-order, pseudo-second order kinetic parameters for Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> adsorption on AC at various initial concentrations**

Metal ions	C <sub>0</sub> (mg L <sup>-1</sup> )	q <sub>e, exp</sub>	Pseudo-first order			Pseudo-second order			
			K <sub>1</sub> × 10 <sup>-3</sup>	q <sub>e, cal</sub>	R <sup>2</sup>	K <sub>2</sub> × 10 <sup>-4</sup>	q <sub>e, cal</sub>	R <sup>2</sup>	h
Pb	50	16.67	9.40	3.03	0.9560	35.08	17.54	0.9992	1.0795
	100	33.01	8.41	4.56	0.9728	12.25	35.21	0.9969	1.5188
	200	63.00	13.72	49.67	0.9901	6.28	67.11	0.9980	2.8304
Cd	50	16.67	5.90	2.97	0.8983	26.30	17.42	0.9969	1.0795
	100	32.33	6.82	4.43	0.9921	9.84	34.72	0.9963	1.1866
	200	62.33	13.63	50.92	0.9902	5.52	66.66	0.9971	2.4515
Ni	50	16.67	6.02	3.11	0.9849	19.90	1.08	0.9969	1.0795
	100	30.33	6.14	4.41	0.9908	9.63	32.89	0.9958	1.0419
	200	59.70	14.23	51.24	0.9877	4.88	64.51	0.9966	2.0329

the adsorption metal ions by AC and their optimal levels are:

- contact time=80 min, pH<sub>0</sub>=7, AC dosage=2 g L<sup>-1</sup>
- initial concentrations of Cd(II), Ni(II) and Pb(II)=100 mg L<sup>-1</sup>

For the maximum sorption of metal ions the concentrations of Cd(II), Ni(II) and Pb(II) metal ions must be at their highest. Therefore, the third level of parameters A, B and C (C<sub>0, Cd</sub>, C<sub>0, Ni</sub> and C<sub>0, Pb</sub>) were used for further calculations. The predicted optimum value of q<sub>tot</sub> for AC was calculated from Eq. (2). The obtained experimental and predicted values are 52.46 and 52.81 (mg/g), respectively.

### 3. Kinetic Studies

The pseudo-first-order and pseudo-second-order kinetic models have been applied for the experimental data to predict to the adsorption kinetics. The pseudo-first-order [20] and pseudo-second-order equations are expressed as:

- simple pseudo first-order kinetic model (Lagergren equation):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

- pseudo second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (10)$$

where q<sub>e</sub> and q<sub>t</sub> are the values of amount adsorbed per unit mass at equilibrium and at any time t, respectively, and k<sub>1</sub> is the pseudo-first order rate constant (min<sup>-1</sup>). The values of k<sub>1</sub> and q<sub>e</sub> can be obtained from the slope and intercept of the linear plot of Ln (q<sub>e</sub> - q<sub>t</sub>) versus t, respectively. Here k<sub>2</sub> is the second order rate constant (g·mg<sup>-1</sup>·min<sup>-1</sup>). The initial adsorption rate, h (mg g<sup>-1</sup>·min<sup>-1</sup>) is expressed as:

$$h = k_2 q_e^2 \quad (11)$$

The plot of t/q<sub>t</sub> versus t gives a linear relationship, which allows computation of k<sub>2</sub>, h and calculated q<sub>e</sub>.

The pseudo-second-order kinetic analysis reveals that the values of the initial adsorption rates, h, increase with increase in the initial metal concentration. The lower the concentration of metal ions in the solution, the lower the probability of collisions between these species is, and hence the faster nickel ions could be bonded to the active sites on the surface of the adsorbent.

According to the correlation coefficients, the pseudo-second-order kinetic model was better than for pseudo-first-order kinetic model (Table 6), and adsorption kinetics can be well explained by the pseudo-

second-order kinetic model for the separation of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> by AC.

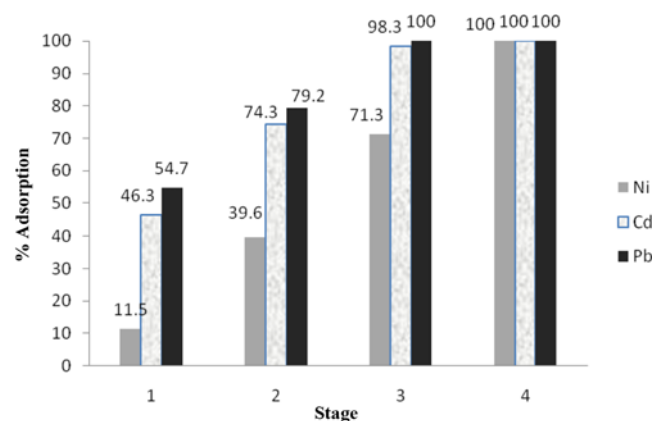
### 4. Multi-stage Adsorption

The results showed that a multi-stage adsorptive treatment would be necessary to reach the minimal discharge standards of metal ions in the effluent. The filtrate acquired from the first stage (after agitating the effluent with AC at optimum dosage) was again treated with fresh adsorbent at optimum conditions dosage in the next stages [22]. The pH<sub>0</sub> of the metal ions solution was adjusted at 7.0 in the stage 1 only. C<sub>0</sub> was taken as 100 mgL<sup>-1</sup> for each metal ion. Multi-stage treatment results for the adsorption of Cd(II), Ni(II) and Pb(II) ions from aqueous solution are shown in Table 7 and Fig. 5.

**Table 7. Multi-stage treatment results**

Concentration (mg L <sup>-1</sup> )	C <sub>Ni</sub>	C <sub>Cd</sub>	C <sub>Pb</sub>
C <sub>0</sub>	100	100	100
C <sup>1.St</sup> *	88.5	53.7	45.3
C <sup>2.St</sup>	60.4	25.7	20.8
C <sup>3.St</sup>	28.7	1.7	-
C <sup>4.St</sup>	-	-	-

\*C<sup>1.St</sup>, C<sup>2.St</sup>, C<sup>3.St</sup>, C<sup>4.St</sup> are indicated remained concentration of metal ion in aqueous solution in 1, 2, 3 and 4<sup>th</sup> stage, respectively



**Fig. 5. Adsorption efficiency of AC during various stages of multi-stage treatment. T=25 °C, t=80 min, C<sub>0</sub>=100 mg L<sup>-1</sup>, m=2 g L<sup>-1</sup>.**

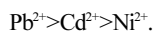
**Table 8. The percentages of metal ions desorption by different extractants in various concentrations**

Metal ion	System	HCl (M)					HNO <sub>3</sub> (M)				
		0.01	0.05	0.1	0.5	1	0.01	0.05	0.1	0.5	1
Pb	Single	21.5	44.9	61.5	72.8	91.5	19.6	48.6	68.9	88.5	100
	Ternary	10.5	25.6	34.7	50.2	79.6	11.7	26.5	37.8	52.4	89.7
Ni	Single	18.9	47.1	63.1	76.8	92.7	20.4	48.7	63.0	78.6	97.4
	Ternary	14.7	28.6	45.9	62.8	83.5	15.9	30.7	49.7	65.6	85.4
Cd	Single	17.8	43.7	54.5	76.7	85.5	20.8	50.9	70.6	90.4	100
	Ternary	13.6	25.8	41.5	60.7	78.6	13.8	27.6	39.7	59.3	82.1

**Table 9. The percentages of adsorption and desorption of heavy metal ions after four successive cycles in single and ternary systems by 1 M HNO<sub>3</sub>**

Cycle No.		Single component system			Ternary component system		
		Pb	Ni	Cd	Pb	Ni	Cd
1	Adsorption (%)	100	89.7	100	87.5	58.9	84.5
	Desorption (%)	100	87.4	100	78.5	50.4	69.4
2	Adsorption (%)	98.4	86.5	97.2	83.6	55.6	83.2
	Desorption (%)	94.6	80.6	92.7	72.3	45.2	66.2
3	Adsorption (%)	96.3	83.8	95.7	77.5	52.8	75.2
	Desorption (%)	88.2	74.2	85.2	63.2	40.3	57.8
4	Adsorption (%)	93.2	81.2	93.1	70.1	48.6	68.8
	Desorption (%)	81.5	68.4	78.1	54.6	35.3	49.9

According to Fig. 5, the sorption capacities for metal ions follow the order:



It suggests that the sorption mechanism depends on the charge electrostatic attraction, hydration energy, hydrated radii of metal and electronic configuration. The comparison of the amounts of individual adsorption capacities has shown that the activated carbon has the lowest affinity towards  $\text{Ni}^{2+}$  ions. However, its adsorption capacity towards  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  is higher and almost the same. The lower adsorption capacity of  $\text{Ni}^{2+}$  ions may be related to the higher hydration energy of this ion compared to the other ones (2,105.0 kJ/mol for  $\text{Ni}^{2+}$  in comparison with 1,500.6 and 1,826.7 kJ/mol for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ ) [35]. It is known that the metal cations are well solvated in water, and before being adsorbed, they should be denuded of their hydration sheath [35,36]. Hydration energy is an important parameter to take into account since the hydrolysis of metal ions occurs by the replacement of water ligands in the inner coordination sphere with hydroxo groups. Adsorption may be related directly to the loss of the outer hydration spheres that precedes hydrolysis. According to these parameters values,  $\text{Pb}^{2+}$  ions will have a greater accessibility to the surface of certain pores than the other metal ions, which would lead to a higher extent in the adsorption process [35]. The other reason of the lower adsorbability towards  $\text{Cd}^{2+}$  compared to  $\text{Pb}^{2+}$  might be the smaller polarizing power of  $\text{Cd}^{2+}$  ions. Thus, the carbon-cadmium interaction forces would be weaker than those between carbon and  $\text{Pb}^{2+}$ .  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  adsorption was not significantly affected by the presence of the other metals, whereas  $\text{Ni}^{2+}$  strongly compete with each other and were displaced in the presence of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .

## 5. Desorption Study

The obtained results for metal desorption from activated carbon are listed in Table 8. As it was expected, all metal ions desorption was increased by increasing in extractant concentration. These results indicated that HNO<sub>3</sub> solution with 1M concentration had the best potential for these metals desorption in single and ternary component systems.

The reusability of activated carbon was investigated by applying AC sample in four successive adsorption/desorption cycles. In these tests, HNO<sub>3</sub> (1M) was used as the extractant. Based on the data in Table 9, the loss of the adsorption percentages from the first to the last cycle for Pb and Cd ions was only about 7% in the single-component systems and about 8.5% for Ni. It indicated that the acid treating could well recover the surface sites occupied by the metal ions; it verifies the key role of the physical sorption in metal adsorption by AC and the formation of relatively weak bonds between the metal ions and AC surface sites.

As expected, the percentages of all metal ions desorption from the saturated AC decreased from the first to the next cycles in single and ternary component systems. It means that after inactivating a part of active sites available easily on the surface of fresh sample in the first cycle, the metal ions may diffuse into the inner structure of AC and adsorb on the new sites with lower accessibilities; therefore, the ability of extractant to recover such occupied sites would be weaker.

The higher losses in the adsorption capacity and percentage of desorption were observed in the ternary system compared to the single-component one. The larger part of the surface sites involved in metal adsorption in ternary systems resulted in the faster rate of adsorbent exhaustion in these systems.



## CONCLUSIONS

Taguchi design method was employed to analyze the adsorption characteristics of three metal ions—Cd (II), Ni (II) and Pb(II)—onto activated carbon. Main adsorption factors such as initial metal ion concentration, pH<sub>0</sub>, adsorbent dose and contact time at three levels with an OA layout of L<sub>27</sub> have been optimized. Maximum sorption for all the metal ions were found to occur at pH<sub>0</sub>=7.0, initial concentration (C<sub>0,i</sub>)=100 mg L<sup>-1</sup>, adsorbent dosage=2 g L<sup>-1</sup> and contact time=80 min. All the factors and the interactions considered in the experimental design with q<sub>eq</sub> as the desired response characteristic are statistically significant at 95% confidence level. The adsorption significance of parameters in multi-component systems falls in the order:

adsorbent dosage > Pb(II) concentration > Cd(II) concentration > contact time > Ni(II) concentration > interaction between (C<sub>0,Ni</sub> & C<sub>0,Cd</sub>) > pH.

Finally, experimental results showed that a multi-staged adsorptive treatment is necessary to reach the minimal discharge standards of metal ions in the effluent.

## REFERENCES

1. K. Kadirvelu, C. Faur-Brasquet and P. Le Cloirec, *Langmuir*, **16**, 8404 (2000).
2. M. Madhava Rao, D. K. Ramana, K. Seshiah, M. C. Wang and S. W. Chang Chien, *J. Hazard. Mater.*, **166**, 1006 (2009).
3. V. C. Srivastava, I. D. Mall and I. M. Mishra, *J. Hazard. Mater.*, **B134**, 257 (2006).
4. P. Senthil Kumar and K. Kirthika, *J. Eng. Sci. Technol.*, **4**, 351 (2009).
5. K. Li and X. Wang, *Bioresour. Technol.*, **100**, 2810 (2009).
6. *Tolerance limits for industrial effluents*, <http://www.worldenviro.com/effstd.htm>.
7. R. C. Bansal and M. Goyal, *Activated carbon adsorption*, Taylor & Francis, USA (2006).
8. D. Mohan and K. P. Singh, *Water Res.*, **36**, 2304 (2002).
9. J. Hanzlik, J. Jehlicka, O. Sebek, Z. Weishauptova and V. Machovk, *Water Res.*, **38**, 2178 (2004).
10. K. Swayampakula, V. M. Boddu, S. K. Nadavala and K. Abburi, *J. Hazard. Mater.*, **170**, 680 (2009).
11. L. Zhi-rong, Z. Li-min, W. Peng, Z. Kai, W. Chuan-xi and L. Hui-hua, *J. China Univ. Mining. Technol.*, **18**, 255 (2008).
12. T. Terdkiatburana, S. Wang and M. O. Tade, *Chem. Eng. J.*, **139**, 437 (2008).
13. B. C. Son, K. Park, S. H. Song and Y. J. Yoo, *Korean J. Chem. Eng.*, **21**, 1168 (2004).
14. M. H. Kasnejad, A. Esfandiari, T. Kaghazchi and N. Asasian, *J. Taiwan Inst. Chem. E.*, **43**, 736 (2012).
15. A. Esfandiari, T. Kaghazchi and M. Soleimani, *J. Taiwan Inst. Chem. E.*, **43**, 631 (2012).
16. H. Shariffard, M. Soleimani and F. Zokaee Ashtiani, *J. Taiwan Inst. Chem. E.*, **43**, 696 (2012).
17. M. Soleimani and T. Kaghazchi, *J. Chin. Inst. Chem. Eng.*, **39**, 9 (2008).
18. T. Kaghazchi and H. Shamsi Jazeyi, *J. Ind. Eng. Chem.*, **17**, 608 (2011).
19. M. Soleimani and T. Kaghazchi, *Bioresour. Technol.*, **99**, 5374 (2008).
20. T. Kaghazchi, N. Asasian Kolar and M. Soleimani, *J. Ind. Eng. Chem.*, **16**, 368 (2010).
21. N. Asasian, T. Kaghazchi and M. Soleimani, *J. Ind. Eng. Chem.*, **18**, 283 (2012).
22. V. C. Srivastava, I. D. Mall and I. M. Mishra, *Ind. Eng. Chem. Res.*, **46**, 5697 (2007).
23. G. Taguchi and R. Jugulum, *The Mahalanobis-Taguchi Strategy*, Wiley, New York (2002).
24. R. L. Mason, R. F. Gunst and J. L. Hess, *Statistical design and analysis of experiments with applications to engineering and science*, Wiley-Interscience, New Jersey (2003).
25. V. C. Srivastava, I. D. Mall and I. M. Mishra, *J. Chem. Eng.*, **140**, 136 (2008).
26. F. Boudrahema, F. Aissani-Benissad and H. Ait-Amar, *J. Environ. Manage.*, **90**, 3031 (2009).
27. V. C. Srivastava, I. D. Mall and I. M. Mishra, *Chem. Eng. Process.*, **47**, 1269 (2008).
28. A. Uccer, A. Uyanik and S. F. Aygun, *Sep. Purif. Technol.*, **47**, 113 (2006).
29. V. C. Srivastava, I. D. Mall and I. M. Mishra, *Colloids Surf., A: Physicochem. Eng. Aspects*, **312**, 172 (2008).
30. R. Roy, *A primer on the taguchi method*, Society Manufacturing Engineers, Dearborn Michigan (1990).
31. N. Gamze Turan, S. Elevli and B. Mesci, *Appl. Clay. Sci.*, **52**, 392 (2011).
32. M. J. K. Bashir, H. Abdul Aziz, M. S. Yusoff and M. N. Adlan, *Desalination*, **254**, 154 (2010).
33. K. Yetilmizsoya, S. Demirel and R. J. Vanderbei, *J. Hazard. Mater.*, **171**, 551 (2009).
34. A. Özer, G. Gürbüz, A. Calimli and B. K. Körbahti, *Chem. Eng. J.*, **146**, 377 (2009).
35. S. Ricordel, S. Taha, I. Cisse and G. Dorange, *Sep. Purif. Technol.*, **24**, 389 (2001).
36. S. B. Chen, Y. B. Ma, L. Che and K. Xian, *Geochem. J.*, **44**, 233 (2010).