Adsorption (2008) 14: 21–29
DOI 10.1007/s10450-007-9042-4

Heavy metal removal using SiO_2-TiO_2 binary oxide: experimental design approach

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Received: 22 February 2006 / Revised: 12 July 2007 / Accepted: 31 July 2007 / Published online: 20 September 2007

Abstract Sorption of Ni^{2+} and Cd^{2+} as heavy metals ions at the interface of the binary oxide TiO_2-SiO_2 was investigated. In addition, physical properties of TiO_2-SiO_2 matrices such as BET surface area, X-ray diffraction, and point of zero charge (pH_{PZC}) were measured. Statistical design of experiments was applied to find the conditions of sorption at which the maximum heavy metal removal was achieved. A second order polynomial function was used to correlate the independent variables (pH, metal ion concentration, and shaking time) and response (heavy metal removal). Values of regression parameters were determined by the computer program, Design expert® (Stat-Ease Inc.). The quality of fit of the polynomial model equation was expressed by the regression coefficient R^2. The sorption results showed that the pH is the most significant factor. In turn, the sorbed percentage reached 100% at high initial concentration and long shaking times due to formation of hydroxyl compounds between the ions and TiO_2-SiO_2 matrices. The results show that there is a Gaussian (normal) distribution of residuals (squared differences between experimentally observed and predicted values from the model), and also that the differences between observed and predicted values are in the range of ±5%. These indicate that experiments were well-conducted and the results have no significant error.

Keywords TiO_2-SiO_2 · Sorption · Heavy metals · Ni^{2+} · Cd^{2+} · Statistical design

1 Introduction

Heavy metals have been a major preoccupation for many years because of their toxicity towards aquatic life, human beings and the environment. As they do not degrade biologically like organic pollutants, their presence in industrial effluents or drinking water is a public health problem due to their absorption and therefore possible accumulation in organisms. As such, they may affect the organisms' structure as well as their functions (Cullen et al. 1983). Several processes have been used and developed over the years to remove dissolved metals from industrial wastewaters such as chemical precipitation, ion exchange, flocculation, reverse osmosis, membrane filtration, or adsorption. Each process from above mentioned processes has its limitations in terms of cost and/or production of toxic derivatives. However, the adsorption process is the most promising technique and attracts the attention of many researchers in this field. Both natural inorganic and organic adsorbent materials have been tested in that regard. For example, different natural oxides were used in heavy metal removal such as: aluminum oxide in Cr^{6+}, Cd^{2+}, and Pb^{2+} removal from wastewaters, geothite or iron oxide coated with sand and clay for Cd^{2+}, and Pb^{2+} removal, and removal of Pb^{2+} compounds using ZnO loaded onto activated carbon (Gupta and Tiwari 1985; Srivastava et al. 1988; Bailey et al. 1992; Potgieter et al. 2006; Kikuchi et al. 2006). On the other

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hand, a great variety of synthetic adsorbents was tested for heavy metal removal (Chakaravarty et al. 2002; Ahluwalia and Goyal 2007; Bailey et al. 1999; Varshney et al. 2007; Jiang et al. 2007). Although many of natural and/or synthetic adsorbents can effectively remove dissolved heavy metals, most of them show some disadvantages such as poor adsorption capacity, a low efficiency/cost ratio, and ineffectiveness for low metal concentrations. Silica gel and TiO_2 represent most of the promising synthetic materials for heavy metal removal by adsorption. Silica gel is a synthetic amorphous polymer that has silanol groups on its surface that allow metal adsorption (Ricordel et al. 2001; Michard et al. 1996). Moreover, the modification of the silica gel surface can be used to enhance its adsorption properties (Tran et al. 1999; Kocjan and Garbacka 1994; Delacour et al. 1999; Bresson et al. 2000). On the other hand, TiO_2-mediated photocatalytic treatment of metal-chelate waste has recently been reported (Chiron et al. 2003; Prairie et al. 1993a, 1993b; Madden et al. 1997). The oxidation process occurs either at the TiO_2 surface or at a small distance from the surface in the solution phase (Davis and Green 1999). Due to the many of advantages of SiO_2 and TiO_2 as sorbents, in the present work, TiO_2-SiO_2 mixed oxide was used as sorbent for removal of heavy metals to get the benefits of both oxides (i.e., the high surface area of silica as well as the photocatalytic ability of TiO_2). To demonstrate practicality, the surface capacity was detected by reusing the mixed oxides many times. Statistically designed experiments, employing the Box Behnken method (Box and Behnken 1960; Cornell and Montgomery 1996), were conducted to determine optimum conditions in terms of pH, shaking time, and metal ions concentrations, as the main process parameters. The results show that this system can remove a high percentage of heavy metals from the solution, as high as 100%.

2 Experimental

2.1 Materials

Titanium (IV), isopropoxide (TIP), and Tetraethyl orthosilicate (TEOS) of analytical grade chemicals were used and $NiCl_2$ (Fischer Scientific) and $CdCl_2$ (Fluka Chemicals) solutions were prepared with deionized water. NaCl (Fisher Scientific) was used for ionic strength adjustment.

2.2 Binary oxide preparation and characterization

TiO_2-SiO_2 was prepared using sol-gel technique by dissolving titanium (IV), isopropoxide (TIIP), and Tetraethyl orthosilicate (TEOS). The conditions of preparation of TEOS: H_2O:C_2H_5OH:HNO_3 (1 M): mole ratios are 1:4:10:0.25 and the TiO_2:$3SiO_2$ mole ratio. TEOS was added to ethyl alcohol (TEOS: ethyl alcohol was 1:10 molar ratio) and H_2O ($1H_2O$:TEOS molar ratio). One ml of HNO_3 0.01 mol dm^{-3} was added to this mixture as a catalyst. The solution was vigorously stirred, and the calculated amount of TIIP was added, and then the remaining water ($3H_2O$:TEOS molar ratio) was added to complete the hydrolysis reaction. The prepared sol was kept at room temperature for gel formation. The gel sample was dried at 103 °C for 18 hours, then at 180 °C for 6 hours and finally at 550°C for 5 hours. The rate of temperature rise was 2 °C/min, which was chosen to obtain TiO_2-SiO_2 xerogel. The surface area of the produced sample was measured using a NOVA 1200 instrument, and was found to be 380 m^2/g. Likewise, X-ray diffraction analysis indicated that the sample is amorphous.

2.3 Sorption tests

All adsorption experiments were conducted using 100-mL plastic bottles in which TiO_2-SiO_2 (5 g/L) was mixed with Ni^{2+} and Cd^{2+} solutions having concentrations ranging from 5 to 10 ppm at 0.05 M NaCl ionic strength. The initial suspension pH varied from 2 to 8 using dilute HCl and $NaBO_4$ (Fisher Scientific). The samples were shaken from 6–24 h to ensure sufficient adsorption time at room temperature (23–25 °C). After equilibration, the suspension pH was measured using an Accumet research AR 50 digital pH analyzer (Fisher Scientific). Subsequently, the suspensions were filtered using 42 filter paper (Whittman). Dissolved Ni^{2+} and Cd^{2+} concentrations were measured using a Perkin-Elmer Optima 3200 RL ICP Emission spectrometer. Determination of the surface charge in terms of zeta potential was measured using ZETA-READER-Mark 21.

2.4 Statistical analysis (Box–Behnken design)

The response surface methodology (RSM) was used to study the simultaneous effects of experimental factors on the heavy metal sorption at TiO_2-SiO_2 surfaces. 3-level-factorial design, employing Box–Behnken design (Box and Behnken 1960; Cornell and Montgomery 1996), was used to identify the optimum region for the dependent variable and to describe the nature of the response surface in the experimental region. As presented in Table 1, factors were prescribed into three levels, coded −1, 0, /and +1 for low,

Table 1 Factors and levels for experimental design using Box Benhken method

Factor	Units	Levels		
		Low (−1)	Mid (0)	High (+1)
Time	Hour	6	15	24
pH	–	2	5	8
Metal ions conc.	ppm	5	7.5	10

Table 2 Box Behnken Design with the 3 levels and 3 variables

Run No.	Coded factor levels			Ions sorbed, %	
	Time, hr	pH	Metal ions conc., ppm	Ni	Cd
1	6.0	2.0	7.5	10.66	17.09
2	6.0	8.0	7.5	100.00	100.00
3	24	2.0	7.5	7.46	12.82
4	24	8.0	7.5	100.00	100.00
5	6.0	5.0	5.0	8.20	11.34
6	6.0	5.0	10	10.10	11.19
7	24	5.0	5.0	8.00	12.22
8	24	5.0	10	10.70	11.56
9	15	2.0	5.0	9.20	14.21
10	15	2.0	10.0	8.80	9.52
11	15	8.0	5.0	100.00	100.00
12	15	8.0	10	100.00	100.00
13	15	5.0	7.5	10.60	16.04
14	15	5.0	7.5	9.73	14.96
15	15	5.0	7.5	9.46	15.70

Stems: Version 3.0 User's Manual. U.S. EPA, Athens, GA (1991)

middle and high levels, respectively. Table 2 represents the design matrix of 15 experiments. For predicting the optimal point, a second order polynomial function was fitted to correlate relationship between independent variables and response (heavy metal removal). For the three factors this equation is:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \sum_{i=1}^{3} \beta_{ij} x_i x_j + \sum_{i=1}^{3} \beta_{ii} x_i^2 \qquad (1)$$

where Y is the predicted response (heavy metal removal) and Xi's are the independent variables (metal ion concentration, shaking time, and pH) that are known for each experimental run. The parameters β_0, β_i, and β_{ij} are the regression parameters. The computer program, Design expert® (Stat-Ease Inc.) was used to perform the statistical analysis of the obtained data. The quality of fit of the polynomial model equation was expressed by the regression coefficient R^2. Experiments were performed in triplicate and mean values are given.

3 Results and discussion

3.1 Zeta potential measurement

The surface sites in terms of neutral and unoccupied surface sites of TiO_2 according to Stone et al. (1993) can be represented as Ti–(OH)(OH_2), having both a surface hydroxyl and a chemisorbed water. Therefore, the acid–base properties of the TiO_2-SiO_2/water interface can be described by

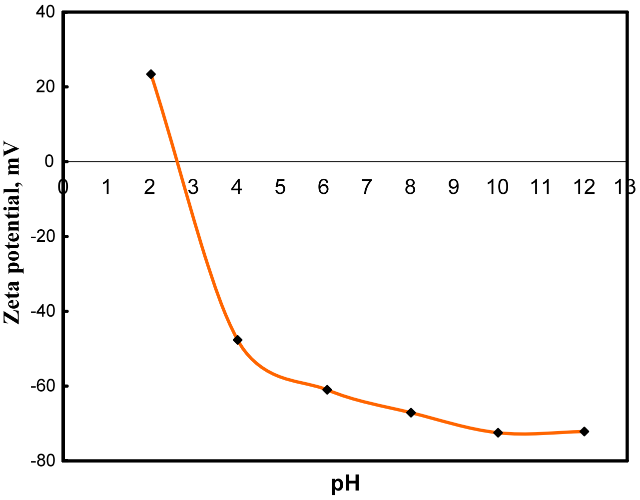


Fig. 1 Zeta potential of binary oxide TiO_2-SiO_2

$$\text{Ti–O–Si–}(\text{OH}_2)_2^+ \rightarrow \text{Ti–O–Si–}(\text{OH})(\text{OH}_2) + \text{H}^+,$$

$$\text{Ti–O–Si–}(\text{OH})(\text{OH}_2) \rightarrow \text{Ti–O–Si–}(\text{OH})_2^- + \text{H}^+$$

where Ti–O–Si–$(OH_2)_2^+$, Ti–O–Si–(OH)(OH_2), and Ti–O–Si–$(OH)_2^-$ are protonated, neutral, and deprotonated titanium dioxide surface sites, respectively.

The above mentioned species, which are function in pH, play an important role of the sorption on the surface of the mixed oxide. Therefore, the effect of pH on the surface species and consequently on the surface charge can be represented by measuring zeta potential of TiO_2-SiO_2. Figure 1 indicates that the PZC of TiO_2-SiO_2, 2.8, is closer to the values of silica's PZC reported in the literature (which ranges from 1.8 to about 3.5 Bresson et al. 2000) than that of titania (which is 6.5). However, the deviation of the PZC value towards the silica value may be due to the high surface area of the silica, which represents most of the binary oxide surface and because of the high Si/Ti (=3) mole ratio employed during synthesis. With the increase of pH from 2 to 10, the zeta potential changes from positively charged at pH below 2.8 to negatively charged above 2.8 as shown in Fig. 1, which indicates presence of the protonated species before pH 2.8, and deprotonated above pH 2.8.

3.2 Preliminary sorption results

Different tests were conducted at different pHs and metal ions concentrations. It is clear from Fig. 2 that the variation of the metal ion concentration has only a slight effect on the sorption, which is not the case with variation of pH. In contrast, it is noticed that the variation of pH significantly affects the sorption of metal ions. Increasing pH from 2 to 8

Fig. 2 Effect of time on the sorption of Ni^{2+} at different pHs and ion concentrations

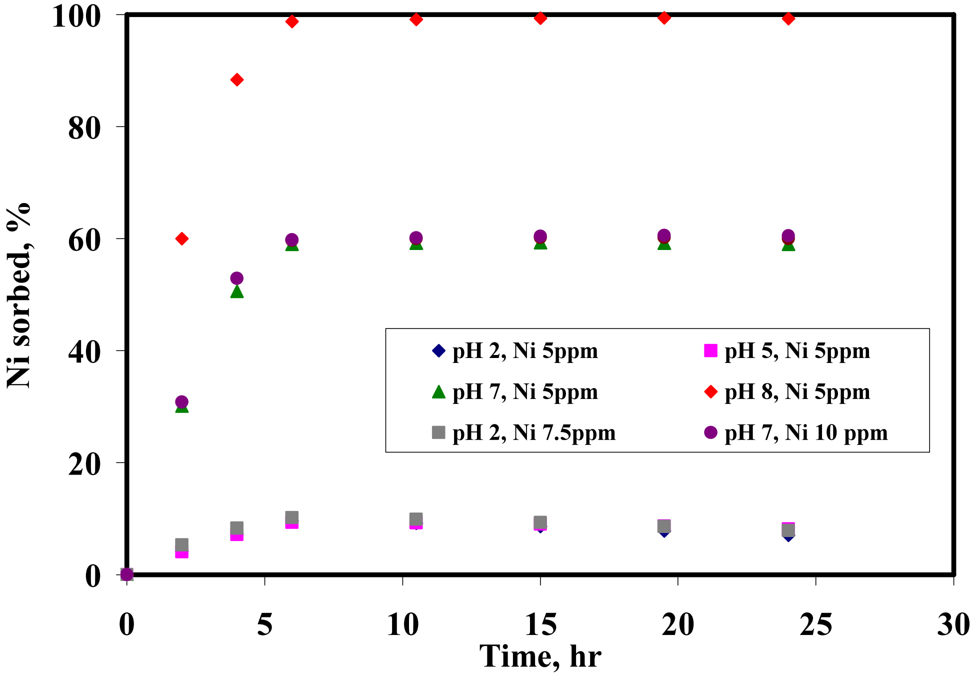
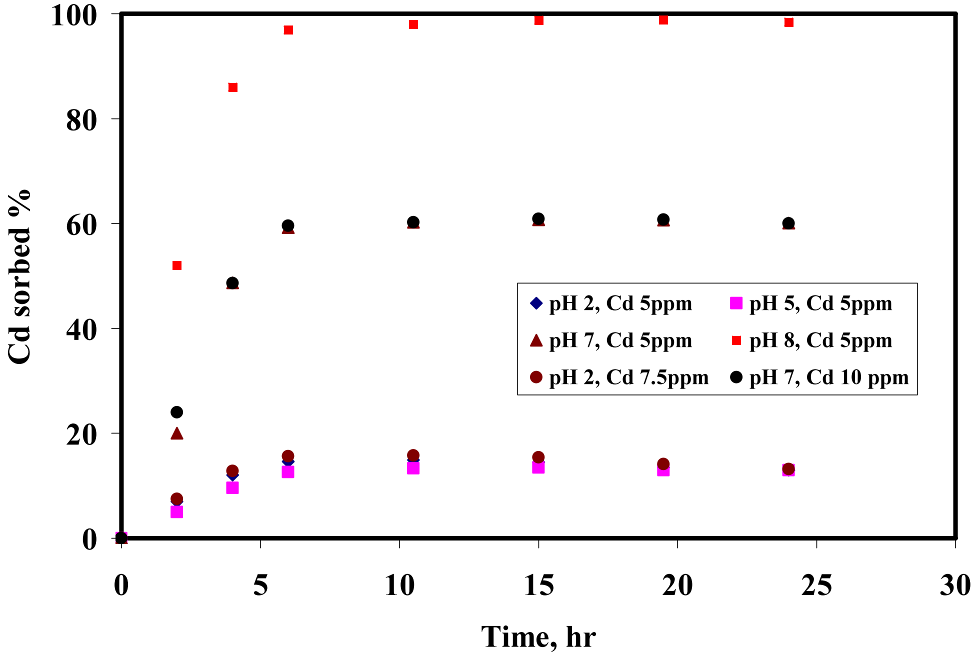


Fig. 3 Effect of time on the sorption of Cd^{2+} at different pHs and ion concentrations



increased the sorption from about 10% to 100%, respectively, as shown in Fig. 2. Additionally, the rate of sorption increases with increasing pH. The same behaviour was noticed in case of Cd^{2+} ions in terms of the amount adsorbed as a function of pH and ion concentration as well as the rate of adsorption, as shown in Fig. 3.

As for any sorption process, it is noticed that there are several factors affecting the heavy metal removal such as pH, ion concentrations, as well as the kinetics, which is apparent by varying the shaking time. To investigate the effect of each factor, statistical analysis was used to optimize the sorption process and to find the interactions among them.

3.3 Optimization of heavy metal removal

An optimization study was conducted to determine the best conditions for separation of heavy metals using binary oxide, in terms of the studied parameters, and to determine

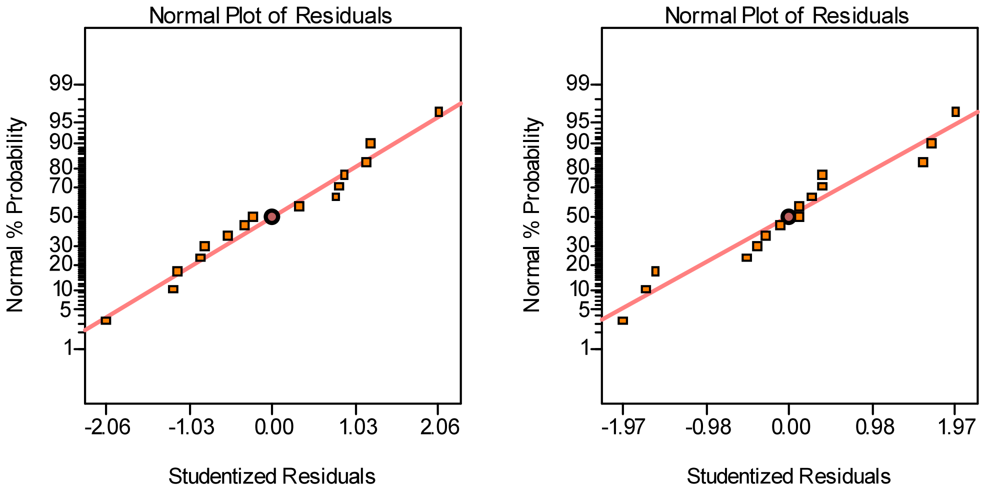


Fig. 4 Predicted versus observed values for the effect of pH, shaking time and metals ion concentration on metal ions sorbed, (**a**) Ni^{2+}; (**b**) Cd^{2+}

the significance of the studied parameters and their effect on the response variable. That is, a 3-level factorial design was used to investigate the simultaneous effect of the time (X1), pH (X2), and metal ion concentration (X3) on the sorption of Ni^{2+} and Cd^{2+} ions and to find the best separation conditions. Table 2 shows the design matrix as well as the results of the response. A multiple regression analysis of the data was used to describe the variables under study. The significance of the equation parameters on heavy metal removal was assessed by the F test.

From Table 2, it is clear that the sorption of Cd^{2+} was higher than that of Ni^{2+} at the same conditions for each run. The sorption of both Ni^{2+} and Cd^{2+} reached 100% at runs no 2, 4, 11, and 12, in which the common factor was the high pH 8. Also, runs no 13, 14, and 15, indicated the magnitude of experimental errors that accompanied this statistical analysis. Figure 4 summarizes the key statistical results of this study. For example, it shows that the standard deviations for Ni^{2+} and Cd^{2+} adsorbed ions were 1.04 and 1.49 and the R^2 values were 0.9998 and 0.9995, respectively.

Firstly, to check the reliability of the statistical analysis, the diagnostic graphs can be used to analyze the data and the typical graph is presented in Fig. 4, which is plot of predicted values as a function of experimentally observed values for sorbed Ni^{2+} and Cd^{2+} when the metal ions concentration, time and temperature are changed. These plots show that there is a Gaussian (normal) relationship between the residuals of the experimentally observed and predicted values from the model, and also that the differences between observed and predicted values are in the range of ±5%. These indicate that experiments were well-conducted and the results have no significant error.

3.3.1 *Effect of pH*

The effect of pH on the surface species is responsible for the adsorption of the ions from the solution. The statistical analysis showed that the pH is the most significant factor. Also, Fig. 5 represents the sorption of the metal ions at different pHs. As can be seen in that figure, the higher the pH, the higher the sorption of the metal ions. At pH 2, the maximum amount sorbed is 30–35% while, by increasing the pH to 8, the adsorbed amount can reach 100%. However, by comparing the extents of sorption at pHs of 2 and 5, there is a small difference in sorbed ion percentages at low initial concentrations. More interesting, the amount of sorbed Ni^{2+} is not less than 98% at pH 8, even at low initial concentration and low shaking time. On other hand, a similar trend was observed in case of Cd^{2+}, where at low pHs (i.e., 2 and 5) the sorption percentage was about 15% while at $pH = 8$ the sorption percentage reached 100%.

As an explanation of sorption behaviour, at high pH, the surface charge of TiO_2-SiO_2 is more negative due to presence of OH^- groups that leads to formation of hydroxyl complexes. Formation of such hydroxyl compounds at higher pH is responsible for the uptake of the metal ions from the solution. The optimum initial pH value was 8 for both Ni^{2+} and Cd^{2+}. In contrast, the low degree of sorption at low pH can be attributed to the competition of cations (Ni^+, Cd^+) and protons (H^+) for the same sites, as well as the repulsion between ions of the same surface charge. The decrease in sorption with increasing the ion concentration at these pHs can be attributed to the limited number of active sites (hydroxylated sites) that can attract the ions from solution. Because of the presence of a nearly neutral surface at $pH = 2$, which is close to the IEP, the sorption is higher than at $pH = 5$.

3.3.2 *Effect of shaking time*

Figure 5 represents contour plots that show the effects of shaking time in terms of Ni^{2+} ions concentration at different pHs. Figures 5(a) and (b) show that as shaking time in-

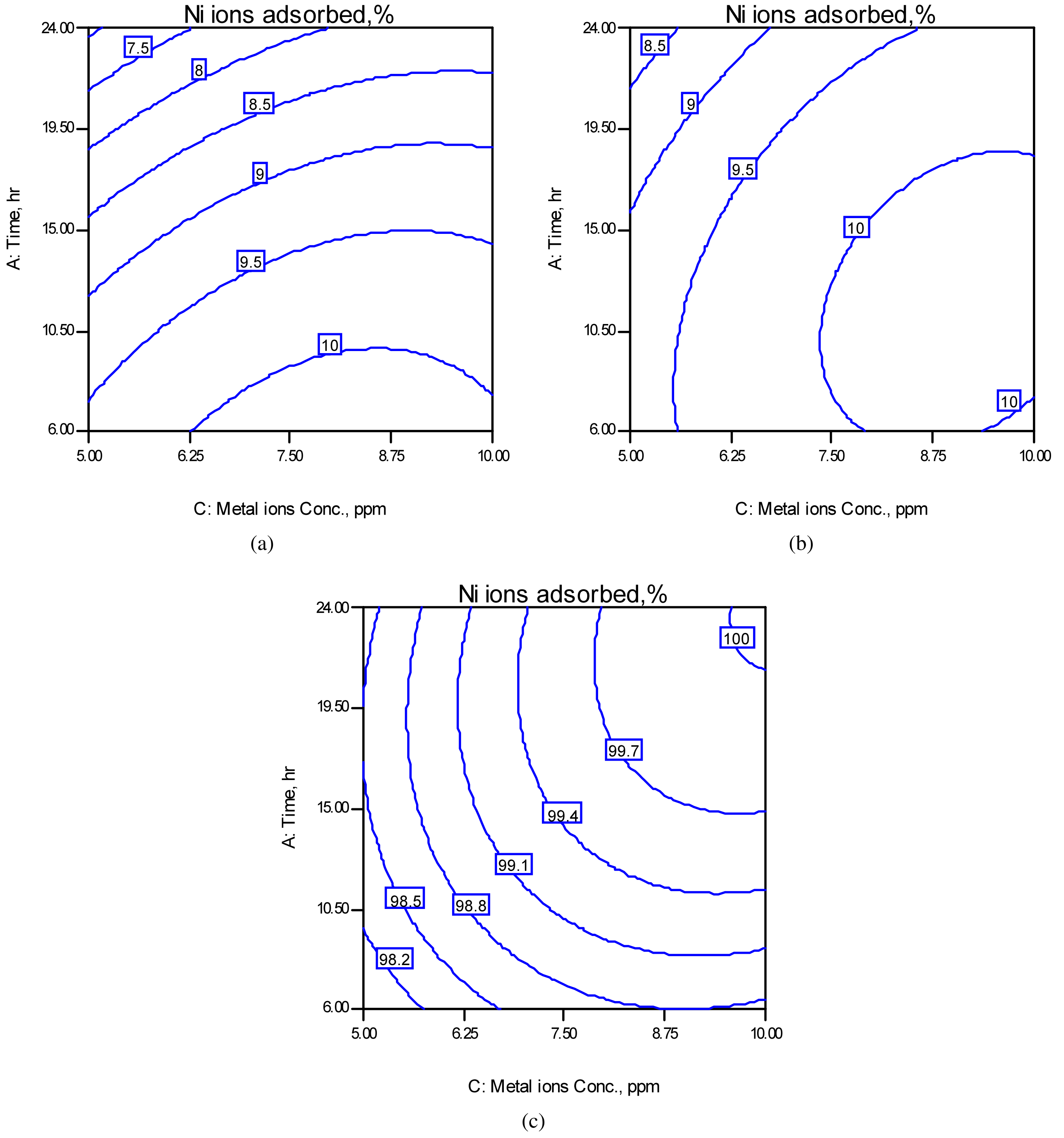
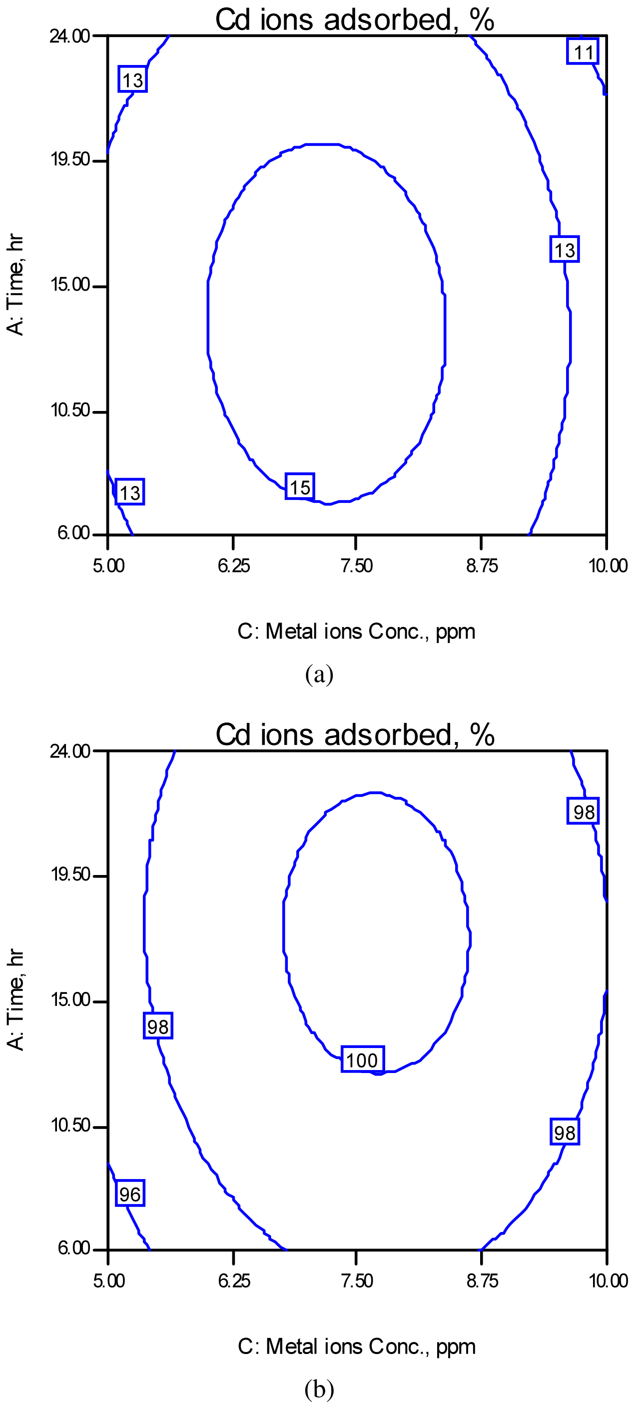


Fig. 5 Contour plots for the effects of Ni^{2+} ions concentration and time on Ni^{2+} ions sorbed (pH = (**a**) 2; (**b**) 5 and (**c**) 8)

creased, the Ni^{2+} ions sorbed decreased from 10 to 7.5%. In contrast, Fig. 5c, reveals that, with increasing shaking time, the amount of sorbed Ni^{2+} ions increased slightly from 98.2 to 100%, at high concentration. The effect of shaking time on the extent of sorption of Cd^{2+} ions is shown in Fig. 6. The effect of shaking time, depicted in Figs. 5 and 6 indicate a slight effect on the sorption of Ni^{2+} and Cd^{2+}, respectively, at low pH, while at higher pH the effect of shaking time is almost negligible.

3.3.3 Ni^{2+} and Cd^{2+} ions concentration

Figure 7 represents a cubic of Box Behnken design which summarizes the results for the sorption of metal ions (a:

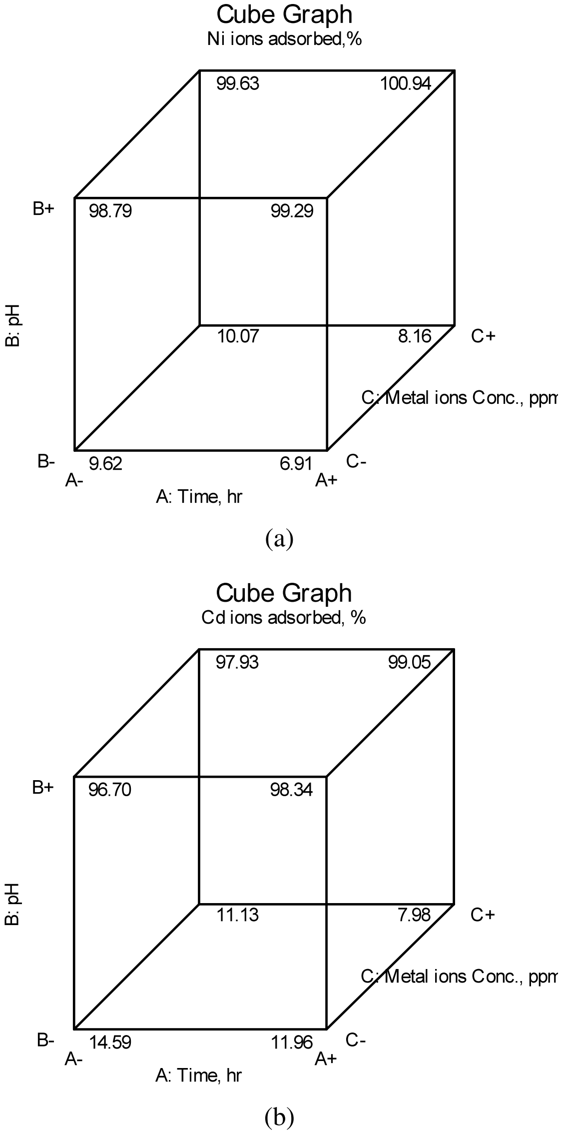


(a)

(b)

Fig. 6 Contour plots of the effects of Cd^{2+} ions concentration and time on Cd^{2+} ions sorbed (pH = (**a**) 5 and (**b**) 8)

Ni^{2+}; b: Cd^{2+}). The results show that the increment of shaking time from low to high level, The Ni^{2+} and Cd^{2+} ions sorbed decreased from 9.62 to 6.91 and from 11.96 to 7.98% respectively. Upon increasing the concentrations of Ni^{2+} and Cd^{2+} ions from low to high, the amount of Ni^{2+} ions sorbed increased from 6.91 to 8.16%, whereas, the amount of Cd^{2+} ions sorbed decreased from 14.59 to 11.96%. In



(a)

(b)

Fig. 7 Cubic representation of the Box Behnken design results for the sorption of metal ions, (**a**) Ni^{2+}; (**b**) Cd^{2+}

contrast, the extent of Ni^{2+} and Cd^{2+} ions sorbed increased from 8 to 100% with increasing pH. It can be concluded that the pH is significant, whereas shaking time and ion concentrations are insignificant. Therefore, the optimum conditions are pH = 8, 10 ppm ion concentration, and 6 hr shaking time for both Ni^{2+} and Cd^{2+}.

3.4 Mechanism of sorption

The findings showed that the extent of adsorption of Cd ions was similar that of Ni ions. For all concentrations of Ni^{2+} and Cd^{2+}, a decrease in pH was observed during the sorption processes, which suggests there was a simultaneous release of H^+ into the solution. It is proposed that the hydroxyl groups of silica, which need alkaline media to be formed, are

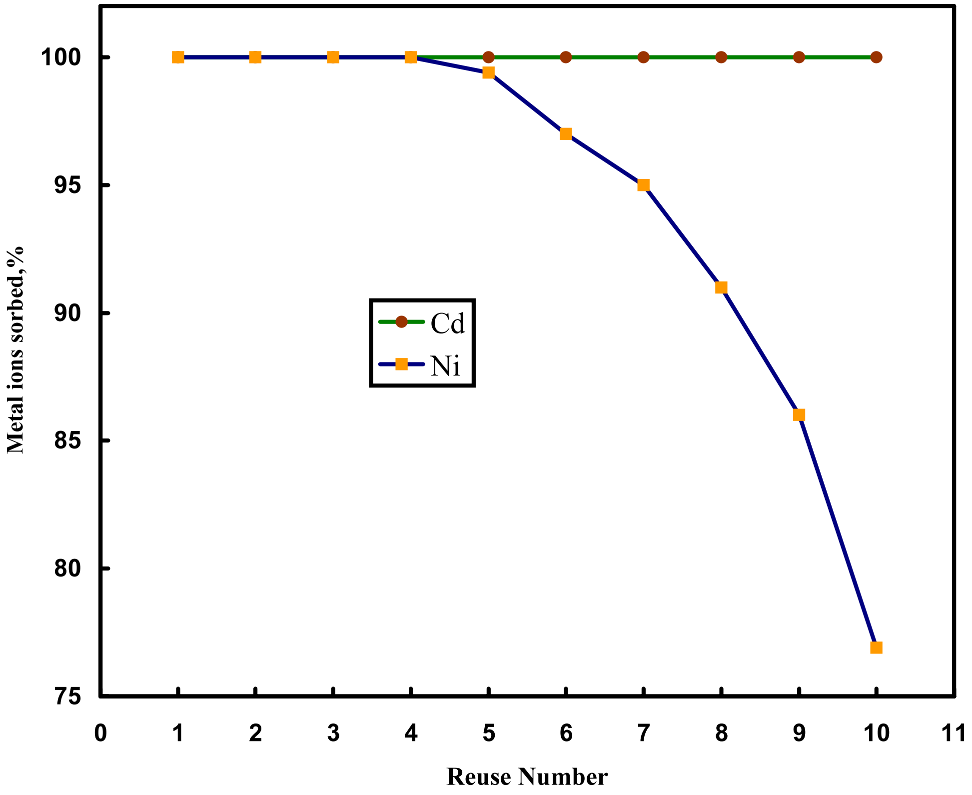


Fig. 8 Effect of reuse TiO_2-SiO_2 on metal ions sorption

involved in the formation of surface complexes with metal ions:

$$\begin{aligned}&\text{Ti–O–Si–OH}(\text{OH}_2) + \text{Ni}^{2+}\\&\quad\rightarrow \text{Ti–O–Si–}(\text{OH}_2)\text{O–Ni}^{+} + \text{H}^{+},\\&\text{Ti–O–Si–OH}(\text{OH}_2) + \text{Cd}^{2+}\\&\quad\rightarrow \text{Ti–O–Si–}(\text{OH}_2)\text{O–Cd}^{+} + \text{H}^{+}.\end{aligned}$$

The binding of Ni(II) and Cd(II) ions by surface functional groups begins at pH 2 and rises steeply to essentially 100% within the next 6 pH units. This suggests that a reaction of Ni^{2+} and Cd^{2+} ions with the TiO_2-SiO_2 surface involves bond formation via surface oxygen atoms and proton release.

Due to the previous results and the effect of the pH on the sorption, it was noticed that the sorption increases with increasing pH from 2 to 8. According to the reaction equations (1), the dominant surface species at this pH is depronotnated OH^-. In addition, the presence of metal ions in forms Ni^+ or NiOH indicates that the possible sorption mechanism is due to hydrogen bond formation. Also, as was indicated in Fig. 6 at $pH = 2$, the extent of sorption is very low. Thus, it is reasonable to look into the speciation of Cd^{2+} and Ni^{2+} at various pH values to obtain a satisfactory explanation. For example, when HCl is used for adjusting the $pH = 2$, chloride ion can react with Cd^{2+} to form anionic complexes such as $[CdCl_3]^-$ etc., which may be extractable or sorbable through an anion exchange mechanism (Groschner and Apriou 1994).

3.5 Reuse experiments

To evaluate the economics of heavy metal removal using mixed oxide, in view of their initial effectiveness, experiments were conducted to assess reusing the particles. Specifically, experiments determined the capacity of the particle surface upon cyclic exposure. The results of these experiments are shown in Fig. 8. Cd^{2+} still was sorbed at 100% after 10 runs while the Ni^{2+} sorption decreased sharply after 6 cycles, and was still dropping after 10 cycles. This is apparently because Cd^{2+} has a higher affinity to form hydroxyl complexes than does Ni^{2+}.

4 Conclusions

The mixed oxide, TiO_2-SiO_2, appears to be a promising substrate for sorption heavy metal ions from solution. The extent of sorption mainly depends on the surface charge as well as the species present in the solution. The main factors affecting the sorption process (i.e., concentration of metal ions, pH, and shaking time) were studied using statistical design of experiments. The resulting statistical analysis shows the pH is the most significant factor. The extent of sorption increases dramatically with increasing the pH. These results can be correlated with the available species in the solution that play a role in forming a surface complexes as well as formation of the hydroxyl compounds at high pHs. The extent of heavy metal removal can reach as high as 100% after 6 hrs shaking time, at either low or high metal concentration, and at high pH, e.g., 8.

References

Ahluwalia, S.S., Goyal, D.: Biores. Technol. **98**, 2243–2257 (2007)

Bailey, R.P., Bennet, T., Benjamin, M.M.: Water Sci. Technol. **26**, 1239–1244 (1992)

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D.: Water Res. **33**(11), 2469–2479 (1999)

Box, G.E.P., Behnken, D.W.: Some new three level designs for the study of quantitative variables. Technometrics **2**, 455–75 (1960)

Bresson, C., Menu, J.M., Dartiguenave, M., Dartiguenave, Y.: J. Environ. Monit. **2**, 240–7 (2000)

Chakaravarty, S., Dureja, V., Bhattacharyya, G., Maity, S., Bhattacharjee, S.: Water Res. **36**, 625–632 (2002)

Chiron, N., Guilet, R., Deydier, E.: Water Res. **37**, 3079–3086 (2003)

Cornell, J.A., Montgomery, D.C.: J. Qual. Technol. **28**, 163 (1996)

Cullen, M.R., Robins, J.M., Eskenazi, B.: Medicine **62**, 221–247 (1983)

Davis, A.P., Green, D.L.: Environ. Sci. Technol. **33**, 609 (1999)

Delacour, L.M., Gailliez, E., Bacquet, M., Morcellet, M.: J. Appl. Polym. Sci. **73**, 899–906 (1999)

Groschner, M., Appriou, P.: Anal. Chim. Acta **297**, 369 (1994)

Gupta, D.C., Tiwari, U.C.: Ind. J. Environ. Health **27**, 205–215 (1985)

Jiang, Y., Gao, Q., Yu, H., Chen, Y., Deng, F.: Microporous Mesoporous Mater. **103**, 316–324 (2007)

Kikuchi, Y., Qian, Q., Machida, M., Tatsumoto, H.: Carbon **44**, 195–202 (2006)

Kocjan, R., Garbacka, M.: Talanta **41**, 131–3 (1994)

Madden, T., Datye, K.A., Fulton, M., Prairie, R.M., Majumdar, A.S., Stange, M.B.: Environ. Sci. Technol. **31**, 3475 (1997)

Michard, P., Guibal, E., Vincent, T., Le Cloirec, P.: Microporous Mater. **5**, 309–24 (1996)

Potgieter, J.H., Potgieter-Vermaaka, S.S., Kalibantonga, P.D.: Min. Eng. **19**, 463–470 (2006)

Prairie, R.M., Evans, R.L., Stange, M.B., Martinez, L.S.: Environ. Sci. Technol. **27**, 1776 (1993a)

Prairie, R.M., Stange, M.B., Evans, R.L.: In: Ollis, D.F., Al-Ekabi, H. (eds.) Photocatalytic Purification and Treatment of Water and Air. Elsevier, Amsterdam (1993b)

Ricordel, S., Taha, S., Cisse, I., Dorange, G.: Sep. Purif. Technol. **24**, 389–401 (2001)

Srivastava, S.K., Bhattacharjee, G., Tyagi, R., Pant, N., Pal, N.: Environ. Technol. Lett. **9**, 1173–1185 (1988)

Stone, T.A., Torrents, A., Smolen, J., Vasudejvan, D.: Environ. Sci. Technol. **27**, 895 (1993)

Tran, H.H., Roddick, F.A., O'Donnell, A.J.: Water Res. **33**(13), 2992–3000 (1999)

Varshney, K.G., Rafiquee, M.Z.A., Somya, A.: Colloids Surf. A: Physicochem. Eng. Aspects **301**, 224–228 (2007)