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ORIGINAL PAPER

FACTORIAL EXPERIMENTAL DESIGN FOR ADSORPTION SILVER IONS FROM WATER ONTO MONTMORILLONITE

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ABSTRACT
This research work involved the use of factorial design technique to investigate the adsorption of silver ions from water onto montmorillonite. There is a growing interest in using low-cost and commercially available materials for the adsorption of heavy metals. Clay particles are strongly anisotropic and exhibit faces and edges, which are very different in surface area and in chemical behavior. It has been reported that the abundance of clay minerals and their low cost has posed them a strong candidate as adsorbent for removal of heavy metal from wastewater. In this study, a factorial experimental design technique was used to investigate the adsorption of silver ions from water onto montmorillonite. The experimental factors and their respective levels that were selected include a pH of 3 – 8, an adsorbent dosage of 0.5–2.0 g/L and an initial silver ions concentration of 20–200 mg/L. The results were analyzed statistically using the Student's *t*-test, analysis of variance, *F*-test and lack of fit to define most important process variables affecting the percentage silver ions adsorption.

KEYWORDS: montmorillonite, factorial design analysis, silver ions adsorption

INTRODUCTION

Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution. The heavy metals, such as lead, copper, cadmium, zinc, silver ions and nickel are among the most common pollutants found in industrial effluents (Stylianou et al., 2007; Nuhoglu and Malkoc, 2009). The presence of the above metals in the environment is of major concern of their toxicity accumulate in living organisms and threat for human life and for the environment, especially when tolerance levels are exceeded (Brasquet et al., 2002; Petrus and Warchol, 2003; El-Kamash et al, 2005). One of the most important heavy metal is silver ions. Silver ions is a naturally occuring transition metal and also a noble metal. Silver ions are generally found in the combined state in nature, usually in copper or lead mineralization (Desai and Murthy, 2012). The major industrial use of silver ions is as silver ions halide in the manufacture of photographic film. Other industrial uses of silver ions include the production of electrical contacts and switching gear, batteries catalysts and mirrors. Free silver ions ion is hazardous to representative species of sensitive aquatic plants and invertebrates (Atia et al., 2005; Akgül et al., 2006). The main technologies used for silver ions removal wastewaters include precipitation, ion exchange, membrane processes, solvent extraction, cementation, electro coagulation, coagulation-flocculation, adsorption, reductive exchange and electrolytic recovery (Chanda et al., 2006; Arous et al., 2004; Top and Ülkü, 2004).

Adsorption has attracted attention because of new material types available for the recovery process. Cost-effective materials that have been investigated for their potential use as adsorbents for heavy metal uptake include sawdust, banana and orange peels, fly ash, red mud, bagasse fly ash, phosphogypsum, bentonite, limestone, waste materials as refuse concrete, zeolite and others (Mier et al., 2001; Annadurai et al., 2002; Taty-Costodes et al., 2003; Weng and Huang, 2004; Kaya and Ören, 2005). Clay minerals are one of the widely studied materials for metal ions extraction and surface modification is often performed to improve the affinity and selectivity in metal ions extraction (Phothitontimongkol et al., 2013).

The evaluation of the best adsorption conditions of metallic ions in different material has been made by several researchers by using a factorial design technique. Most studies on heavy metal adsorption by clay minerals have used the "one variable at a time" strategy that tacitly assumes that the variables are independent. Usually this is not true, and in these cases it is necessary to consider several factors simultaneously (Echeverría et al., 2005). The analysis in which the evaluation of more than one factor can be done is called full factorial analysis. This study illustrates the use of montmorillonite as natural low cost adsorbent for the adsorption of silver ions and optimization of various parameters influencing the adsorption efficiency using 2^3 full factorial design.

Table 1 The chemical composition of montmorillonite.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	TiO_2	NaO_2	MnO	Cr_2O_3	P_2O_5	LOI[a]
w %	57.8	17.7	7.9	2.4	1.6	1.5	0.8	0.5	0.3	0.1	<0.1	9.05

[a]Loss on ignition

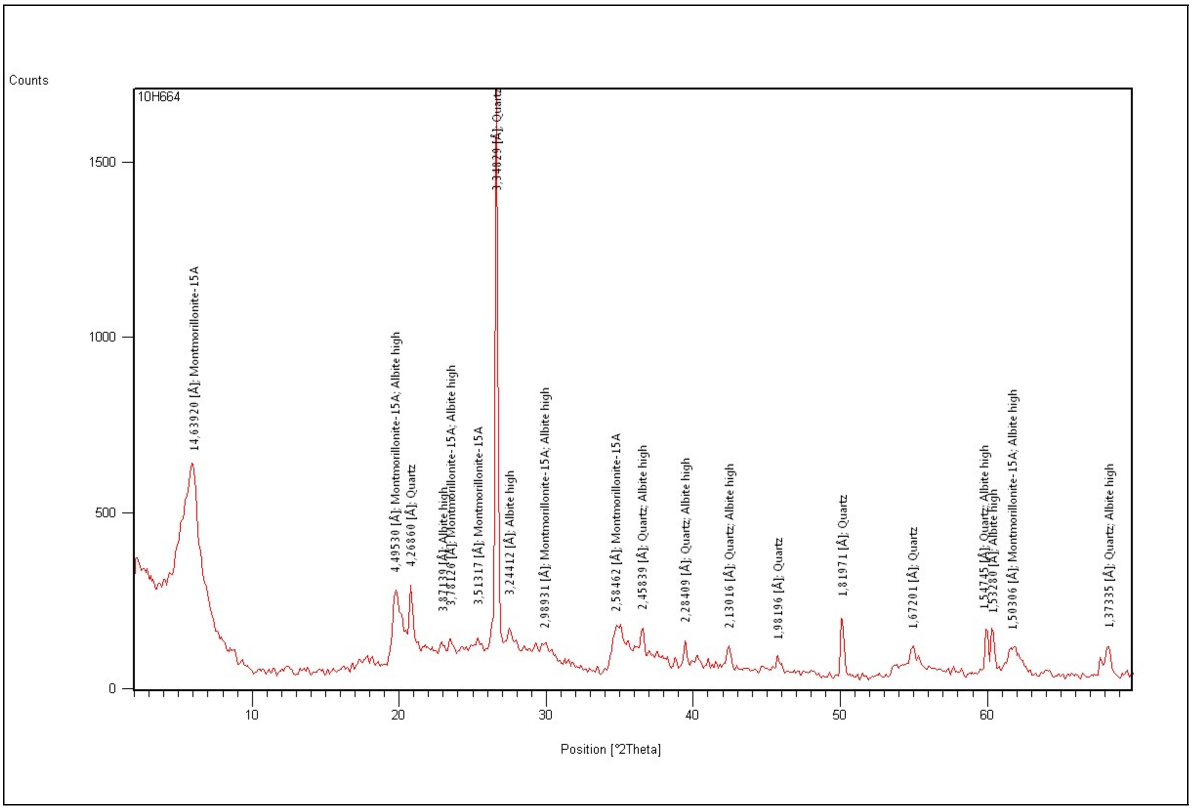

Fig. 1 XRD pattern of montmorillonite.

MATERIALS AND METHODS

MATERIALS

The montmorillonite, used in the experiments was supplied from the Bafra in Turkey. It contains various amounts of smectite, quartz, feldspar group and amorphous material, which is a kind of montmorillonite. The chemical composition of the montmorillonite was given in Table 1. Major elements of montmorillonite were determined by XRF spectrometer. The formation of a new structure was determined by the peak internal between 2.5^o – 70^o in the XRD pattern montmorillonite (Fig. 1). The specific BET surface area of montmorillonite was measured with nitrogen as 73.916 m^2/ g. Electron Scanning (SEM) image for natural clay is shown in Figure 2.

METHOD

Natural montmorillonite, grey in color was used as an adsorbent. It was dried, and then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried at 105 ^{o}C in an oven before use in the adsorption studies. All adsorption experiments were carried out with the batch method. Adsorption properties of montmorillonite were evaluated by depending on different adsorption conditions such as different pH, adsorbent dosage and initial silver ions concentrations. After the adsorption period, the mixtures were filtered with 0.45 μm filter and acidified with HNO_3 to decrease the pH to below 2 before the AAS measurement. The adsorption percentage of silver ions was calculated by the difference of initial concentration using the equation expressed as follow:

$$R = \frac{C_o - C_e}{C_o} x100 \quad (1)$$

where C_o is the initial concentration of silver ions solution (mg/L), C_e the equilibrium concentration of the silver ions solution (mg/L), and R is the retention of silver ions in % of the added amount.

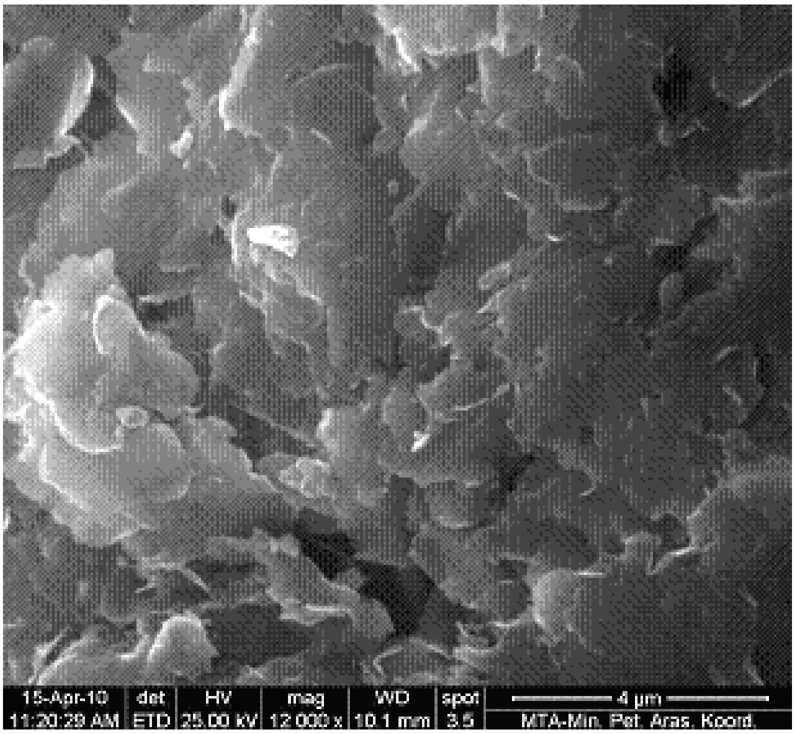

Fig. 2 SEM image for montmorillonite.

Table 2 Factors and levels used in the factorial design.

Factor	Coded Symbol	Low Level (-1)	High Level (+1)
pH	*A*	3	8
Adsorbent Dosage (g/L)	*B*	0.5	2
Initial Concentration (mg/L)	*C*	20	200

FACTORIAL EXPERIMENTAL DESIGN

Factorial design is employed to reduce the total number of experiments in order to achieve the best overall optimization of the system. It was used to reduce the number of experiments, time, overall process cost and to obtain better response (Lima et al., 2011). The design determines that factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. The number of experimental runs at b levels is b^k, where k is the number of factors (Navidi, 2008). Today, the most widely used kind of experimental design, to estimate main effects as well as interaction effects, is the 2^p factorial design in which each variable is investigated at two levels (Kavak, 2009).

The high and low levels defined for the 2^3 factorial designs were listed in Table 2. The low and high levels for the factors were selected according to some preliminary experiments. The order in which the experiments were made was randomized to avoid systematic errors. The results were analyzed with the Minitab 16 software, and the main effects and interactions between factors were determined. The 2^3 factorial design cubical diagrams with high and low three factors, pH adsorbent dosage and initial concentration is shown in Figure 3. Figure 3 illustrates the mean of the experimental results for the respective low and high levels of adsorbent dosage, initial concentration and pH.

RESULTS AND DISCUSSION

A 2^3 full factorial design (three factors each, at two levels) was employed to evaluate the importance and interactions of the pH, adsorbent dosage and initial silver ions concentration. The response variables in this study are the adsorption efficiency of silver ions.

The factorial design matrix and adsorption efficiency (%) measured in each factorial experiment is shown in Table 3, with the low (−1) and high (+1) levels as specified in Table 2. Factors that influence the adsorbed quantity of silver ions adsorbed onto

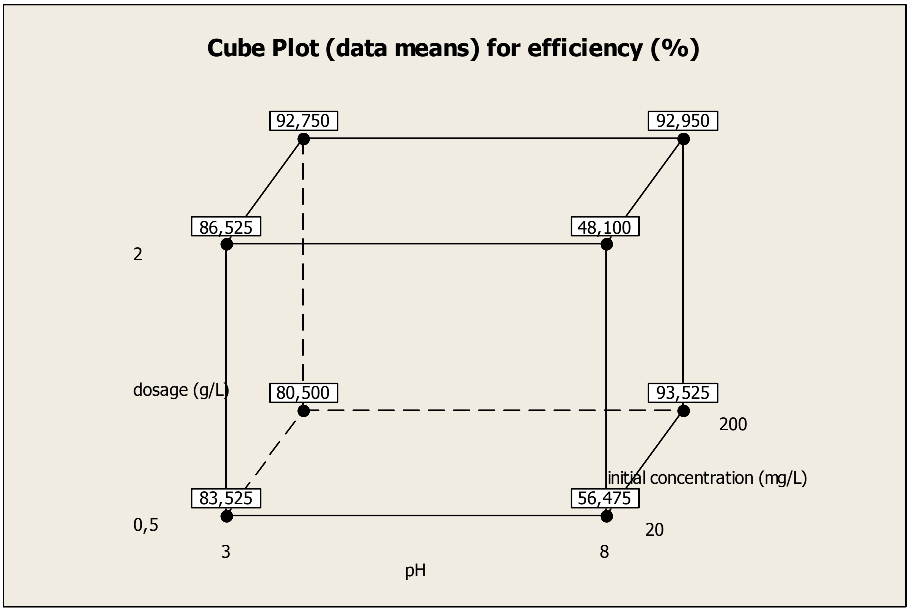

Fig. 3 Cube plots for adsorption efficiency (%).

Table 3 Design matrix and the results of the 2^3 full factorial design.

Run No	A	B	C	Average (adsorption efficiency %)
1	-1	-1	-1	83.525
2	+1	-1	-1	56.525
3	-1	+1	-1	86.525
4	+1	+1	-1	48.100
5	-1	-1	+1	80.500
6	+1	-1	+1	93.525
7	-1	+1	+1	92.75
8	+1	+1	+1	92.85

montmorillonite were evaluated by using factorial plots: main effect and normal probability plots. ANOVA and P-value significant levels were used to check the significance of the effect on adsorption efficiency (%). The results of the experimental data were studied and interpreted by Minitab 15 statistical software.

The results were displayed in Tables 4 and 5. Main and interaction effect, coefficients of the model, standard deviation of each coefficient, and probability for the full 2^3 factorial designs were presented in Table 4. The significance of the regression coefficients was determined by applying a Student's t-test. All effects were significant with 95% confidence level. In addition, the model presented an adjusted square correlation coefficient R^2 (adj) of 100.00 %, fitting the statistical model quite well. In this way, the silver ions uptake by montmorillonite could be expressed using the following equation (2) :

$$\begin{aligned} R(\%) &= 79.294 - 6.531 \cdot pH - 0.787 \cdot Dosage + \\ &+ 10.637 \cdot Concentration - 3.025 \cdot pH * Dosage + \\ &+ 9.837 \cdot pH * Concentration + \\ &+ 2.131 \cdot Dosage * Concentration - \\ &- 0.181 \cdot pH * Dosage * Concentration \end{aligned} \tag{2}$$

Table 5 shows the sum of squares being used to estimate the factors effect and the *F*-ratios, which are defined as the ratio of respective mean-square-effect to the men-square-error. The significance of these effects was evaluated using the t-test, and had a significance level of 5 %; i.e., with a confidence level of 95 %. The *R*-squared statistic indicated that the first-order model explained 99.99 % of R's variability to the rejection of null hypothesis, it appears that the main effect of each factor and the interaction effects were statistically significant: $P<0.05$ (Abdel-Ghani et al., 2009). The results revealed that the studied factors (A, B and C), their 2-way interaction (AB, AC and BC) and 3-way interaction (ABC) were statistically significant to *R (%)*.

The main effects of each parameter on the silver ions adsorption are shown in Figure 4. It shows only the factors that were significant at the 95% confidence interval. Figure 4 shows that significance effect upon efficiency have the control factors: pH, adsorbent dosage and initial concentration. The main effect plots in Figure 4 are helpful in visualizing which factors most affect the response. Each level of the factors affects the response (i.e., adsortion efficiency) differently. If the slope is close to zero, then the magnitude of the main effect would be small. pH factors at their low level result in higher mean

Table 4 Estimated effects and coefficients for adsorption efficiency.

Estimated effects and coefficients for efficiency (%) (coded units)

Term	Effect	Coef	SE Coef	*T*	*p*
Constant		79.294	0.02073	3825.27	0.000
pH	-13.062	-6.531	0.02073	-315.08	0.000
dosage (g/L)	1.575	0.787	0.02073	37.99	0.000
initial concentration (mg/L)	21.275	10.637	0.02073	513.17	0.000
pH*dosage (g/L)	-6.050	-3.025	0.02073	-145.93	0.000
pH*initial concentration (mg/L)	19.675	9.837	0.02073	474.58	0.000
dosage(g/L)*initial concentration(mg/L)	4.263	2.131	0.02073	102.82	0.000
pH*dosage(g/L)* initial concentration(mg/L)	-0.363	-0.181	0.02073	-8.74	0.000

S = 0.0829156 PRESS = 0.22
R-Sq = 100.00 % R-Sq(pred) = 99.99 % R-Sq(adj) = 100.00 %

Table 5 Analysis of variance for adsorption efficiency.

Analysis of variance for efficiency (%) (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	P
Main Effects	3	2502.94	2502.94	834.31	0.000
pH	1	682.52	682.52	682.52	0.000
dosage (g/L)	1	9.92	9.92	9.92	0.000
initial concentration (mg/L)	1	1810.50	1810.50	1810.50	0.000
2-Way Interactions	3	1767.51	1767.51	589.17	0.000
pH*dosage (g/L)	1	146.41	146.41	146.41	0.000
pH*initial concentration (mg/L)	1	1548.42	1548.42	1548.42	0.000
dosage (g/L)*initial concentration (mg/L)	1	72.68	72.68	72.68	0.000
3-Way Interactions	1	0.53	0.53	0.53	0.000
pH*dosage (g/L)*initial concentration (mg/L)	1	0.53	0.53	0.53	0.000
Residual Error	8	0.05	0.05	0.01	
Pure Error	8	0.05	0.05	0.01	
Total	15	4271.03			

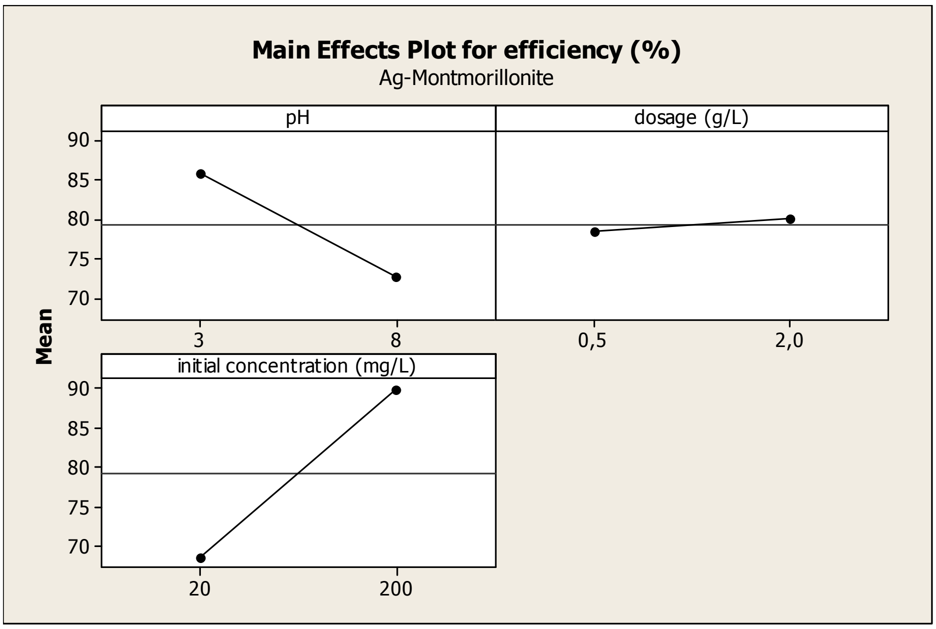

Fig. 4 Main effect plots for efficiency (%).

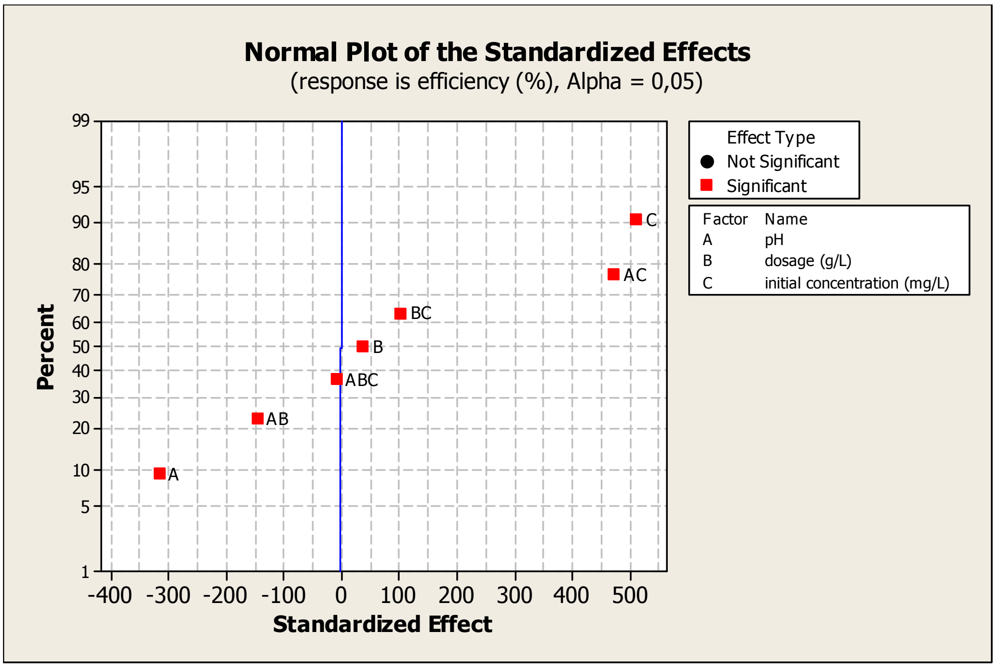

Fig. 5 Normal probability plot of standardized effects.

responses compare to that at the high level. For adsorbent dosage and initial concentration factors, the reverse is true. Additionally, the factor A appears to have a greater effect on the response, as indicated by a steeply slope.

The solution pH is one of the parameters that has strong influence on metal adsorption due to the presence of different metal species in solution at different pH (i.e. metal ions and/ormetal hydroxide precipitate) and the protonation or deprotonation of ligand active sites that would affect the binding ability with metal species. Moreover, wastewater would have different pH depending on the source. Hence, it is necessary to observe the adsorption behavior of the adsorbents to facilitate the use in the real situation. The efficiency in silver ions adsorption from solution by clay mineral was significantly improved when it was functionalized with montmorillonite. In strong acid solution, the surface hydroxyl groups would not dissociate and therefore, the adsorption of Ag+ species could rarely occur. When the solution pH increased, the surface became deprotonated and negatively charged and the uptake of silver ions was observed. However, the amount of adsorbed silver ions was small due to the competitive adsorption with other salts in solution (i.e. NaNO3). The solution pH would affect the amount of silver on clay surface. The adsorption capacity generally increased when the initial pH of solution was increased. In the experimental conditions described above, four different simple retention processes can take place (Alvarez-Puebla et al, 2004; Phothitontimongkol et al., 2013):

Process 1.
Electrostatic retention of the cation $[M(H_2O)_6]^{2+}$

$$S\text{-}H + [M(H_2O)_6]^{2+} \rightarrow SH\text{-}[M(H_2O)_6]^{2+} \quad (3)$$

Process 2.
Surface complexation of the cation $[M(H_2O)_6]^{2+}$

$$2S\text{-}H + [M(H_2O)_6]^{2+} \rightarrow [MS_2(H_2O)_4] + 2H_3O^+ \quad (4)$$

Process 3.
Surface complexation of the cation $[M(OH)(H_2O)5]^+$

$$S\text{-}H + [M(OH)(H_2O)_5]^+ \rightarrow [MS(OH)(H_2O)_4] + H_3O^+ \quad (5)$$

Process 4.
Precipitation of $M(OH)_2$ on the solid surface

$$[M(H_2O)_6]^{2+} + 2OH^- \rightleftarrows M(OH)_2\downarrow + 6H_2O \quad (6)$$

The dosage has a very weak positive effect upon responses. The initial concentration has a strong positive influence upon adsorption process efficiency. These conclusions are in a strong correlation with the results obtained from the adsorption studies.

It is not clear whether these results are "real" or "chance". To identify the "real" effects, a normal probability plot is used. One point on the plot is assigned to each effect. According to the normal probability plots, the points which are close to a line fitted to the middle group of points represent those estimated factors that do not demonstrate any significant effect on the response variables. Points far away from the line likely represent the "real" factor effects (Brasil et al., 2006; Palanikumar and Dawim, 2009).

The normal probability plot was given in Figure 5. The main factors (A, B, and C) and their interactions (AB, AC, and BC) are very far away from the straight line and are therefore considered to be "real". Because A, AB, and ABC lie to the left of the line, their contribution had a negative effect, B, C, AC, and BC on the right had a positive effect. The initial concentration (C) had largest effect because its point lies farthest from the line. These results confirm the previous the values of Table 4. The effects decreased as C>AC>A>AB>BC>B>ABC.

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CONCLUSION

The present investigation shows that montmorillonite is an effective adsorbent for adsorption of silver ions. The effects of process parameters such as pH, montmorillonite dosage and initial concentration were studied. The most significant effect was found to be initial concentration. Then pH- initial concentration of silver ions interaction, pH, pH-montmorillonite dosage of silver ions interaction, montmorillonite dosage-initial concentration of silver ions interaction, montmorillonite dosage and pH-montmorillonite dosage-pH of silver ions interaction were also found highly significant. The adsorption process can be applied in acidic media. The statistical design of the experiments combined with techniques of regression was applied in optimizing the conditions of maximum adsorption of the silver ions onto montmorillonite. ANOVA indicated that the most considerable factor was pH for silver ions. Individual, two and three ways interactions were also significant.

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