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ORIGINAL PAPER

REMOVAL OF CU^{2+} FROM COPPER FLOTATION WASTE LEACHANT USING SEPIOLITE: FULL FACTORIAL DESIGN APPROACH

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ABSTRACT
Copper flotation waste which is the product pyrometalurgical production of copper from copper ores contains materials such as iron, alumina, calcium oxide, silica, etc. Copper flotation waste generally contains a significant amount of Cu together with trace elements of other toxic metals such as Zn, Co and Pb. A variety of techniques can be used for decontaminating and remediating copper slag. Environmental remediation technologies include in situ or ex situ techniques for decontaminating the polluted fields, such as soil-washing, physical separation, phytoremediation and leaching. The aim of the present study is to investigate the removal of the copper from copper flotation waste leachant using sepiolite. 2^3 full factorial design was employed to study the effect of three factors which are contact time, adsorbent dosage and pH at two levels.

KEYWORDS: copper flotation waste, leaching, copper, sepiolite, full factorial design

INTRODUCTION

Copper is one of the oldest metals used and has been one of the important materials in the development of civilization. The most important types of copper ores are the sulfides, oxides and carbonates. Copper is recovered either pyrometallurgically or hydrometallurgically. Prometallurgy, or smelting, is used on ore with copper sulfide and iron sulfide minerals. The concentrate is dried and fed into a furnace. The minerals are partially oxidized and melted, resulting in segregated layers. The matte layer refers to the iron-copper-sulfide mixture which sinks to the bottom. The slag, which refers to the remaining impurities, floats on top of the matte. The copper flotation waste (slag) generated from the copper industry is a by-product from the copper smelting industry. Landfill disposal of copper industry waste is not feasible since a few hundred tons are produced per year per factory; leaching of heavy metals in the ground water is of concern (Singh, 2002; Gorai et al., 2003; Hietala and Varien, 2003). The toxicity of the waste is determined by leaching tests and depending on the chracteristics of the waste the spent abrasive must be disposed of as solid or hazardous waste**.** More recently, several studies have been conducted using the untreated or variously stabilized red mud residues from metallurgical treatment of bauxite ores, clays, zeolite, fly ash produced by coal-fired power stations and bagasse fly ash generated by the sugar industry (Ciccu et al., 2003; Bertochi et al., 2005; Çoruh, 2008; Mohan and Gandhimathi, 2009).

Sepiolite ($(Si_{12}O_{30}Mg_8(OH)_4(H_2O)_48H_2O)$) is a natural, fibrous clay mineral with fine microporous channels with dimensions of 0.37x1.06 nm running parallel to the length of the fibers. Sepiolite is often found associated with other clay and non-clay minerals such as carbonates, quartz, felsdpar and phosphates. The most important occurrences of sepiolite are found in Vallecas of Spain, Turkey, Madagascar and Tanzania (Ozdemir et al., 2009; Işık et al., 2010). Thus it is important characterize this clay mineral and evaluate how important physicochemical properties are altered during chemical and thermal treatment (Balci, 2004; Uğurlu, 2009). This mineral is widely used to remove undesired components from household and industrial wastewaters and in various industrial manufacturing processes, such as removing some organic matters from wastewater, heavy metals, ammonium and phosphate, color and other undesirable components, dyes, phenol, and lignin. Studies conducted recently showed that sepiolite can retain a significant amount of Cu(II), Zn(II), Cd(II), Co(II) and Pb(II) ions from aqueous solutions (Kocaba and Akyüz, 2005; Kilislioglu and Aras, 2010).

Adsorbent dosage, initial pH and contact time are important parameters in adsorption. In this study, we investigated the adsorption properties of sepiolite by varying these factors at two levels. Interaction between these factors were studied and optimization done.

MATERIALS AND METHODS

MATERIALS

Copper flotation waste

Copper flotation waste has a black color and glassy appearance. The specific gravity of copper flotation waste is 3100 kg/m^3. The chemical composition of copper flotation waste is given in Table 1

Sepiolite

Sepiolite sample was obtained from Aktaş Lületaşı Co. in Eskişehir, Turkey. Prior to batch adsorption experiments, the sepiolite was washed with distilled water in order to remove the surface dust and dried at 103 ^{o}C. The chemical compositions of sepiolite are given Table 1.

Table 1 Chemical composition (wt. %) of copper flotation waste and sépiolite.

	Copper flotation waste	Sepiolite
SiO_2	24.87	53.47
Fe_2O_3	67.68	0.16
Al_2O_3	0.92	0.19
CaO	0.69	0.71
CuO	0.98	-
ZnO	2.78	-
PbO	0.21	-
Cr_2O_3	0.12	-
SO_3	2.18	-
MgO	0.36	23.55
CoO	0.21	-
LOI*	-	21.49

*Loss on ignition

TCLP Leaching test

Several leaching procedures have been developed to simulate the leaching processes of hazardous wastes in landfills or natural environments in order to evaluate the possibility of human health hazard threats from the tested wastes. The TCLP test, widely used by state and national agencies, was designed to simulate leaching of heavy metals and organics from industrial wastes to be codisposed in landfills. For this reason, TCLP test method was used to evaluate the leaching and pollution potentials of pollutants in the waste in this study. The TCLP test involves the extraction of contaminants from a 100 g size-reduced sample of waste material with an appropriate extraction fluid. The extraction fluid used for the extraction depends on the alkalinity of the waste material. Very alkaline waste materials are leached with a fixed amount of acetic acid without buffering the system (pH 2.88), while other waste materials are leached with acetic acid buffered at pH 4.93 with 1 N sodium hydroxide. A 20:1 liquid to solid (L/S) ratio (mass/mass, m/m) is employed, and the mixture is rotated for 18 h at 30 rpm using a rotary agitation apparatus (USEPA, 1990; Kim, 2003; Cohen and Petria, 2005). The concentration of copper in industrial leachate was 140.9 mg L^{-1}, indicating that it is much higher than limit values established in Turkish and EPA standards.

METHOD

Adsorption studies are carried out under different experimental variables including adsorbent dosage, solution pH, contact time, ionic strength, temperature, particle size and solute concentration. The main reason of studying such a large number of variables is to locate the best conditions for best adsorption. To test the conventional methods used to determine the influence of each one of these factors, experiments were carried out by systematically varying the studied factors and keeping constant the others. This should be repeated for every influence factors, resulting in an unreliable number of experiments. Factorial designs are widely used to investigate the effects of experimental factors and the interactions between those factors in a response. The advantages of factorial experiments include relatively low cost, a reduced number of experiments, and increased possibilities to evaluate interactions among the variables (Al-Degs, 2012; Tekbaş, et al., 2009).

In this study, a Full Factorial Design of Experiment was designed to investigate the effect of contact time, initial pH and adsorbent dosage on the removal of copper with sepiolite. The samples were mixed at predetermined periods at a temperature of 20 ^{o}C in a shaker at 155 rpm until equilibrium was reached. After equilibrium, the mixtures were filtered with 0.45 µm filter and acidified with HNO_3 to decrease the pH to below 2 before measurement. The copper metal concentration in the filtrate was determined using AAS (Atomic Absorption Spectrophotometry).

Table 2 The levels of experimental factor.

Factor	Low Level (-1)	High Level (+1)
Contact Time (min.) (***A***)	10	120
Adsorbent Dosage (g/L) (***B***)	5	30
Initial pH(***C***)	3	8

Table 3 Experimental Design Matrix of Copper Removal.

Run No.	Factor			Removal (%)
	A	B	C	
1	-1	-1	-1	13.25
2	+1	-1	-1	23.19
3	-1	+1	-1	51.38
4	+1	+1	-1	61.02
5	-1	-1	+1	98.40
6	+1	-1	+1	98.65
7	-1	+1	+1	99.85
8	+1	+1	+1	99.92

Full Factorial Design of Experiments examines every possible combination of factors at the levels tested (George et al., 2005). The general notation for a full factorial design run at *b* levels is b^k=# runs, where *k* is the number of factors. The 2^3 factorial design with high and low levels of factors are given in Table 2 (*b*=2 and *k*=3).

In a 2^3 full factorial design, there are eight runs or combinations. The results of each run with duplicate tests are shown in Table 3. The best combination of the factors for the maximum copper removal efficiency occurs at run 8.

RESULTS AND DISCUSSION

The parameters involved in the adsorption experiments were optimized by full factorial design (2^3) using statistical software MINITAB (Version 15). In this investigation for quantification of the effects of the three variables on the cupper removal, a two level factorial design of experiments was adopted. Factors that influence the adsorbed quantity of copper adsorbed onto sepiolite were evaluated by using factorial plots: main effect and interaction effect. *ANOVA* and *P*-value significant levels were used to check the significance of effect on removal (%).

ANOVA

The results were displayed in Tables 4 and 5. Main, interaction effect, coefficients of the model, standard deviation of the each coefficient, and probability for the full 2^3 factorial designs were presented in Table 4. The significance of the regression coefficiens was determined by applying a Student's *t*-test. All effects were significant with 95 % konfidence level. In addition, the model presented an adjusted square correlation coefficient R^2 (adj) of % 100, fitting the statistical model quite well. In this way, the copper uptake by sepiolite could be expressed using the following equation:

$$\text{Removal}(\%) = 68.209 + 2.482 \times \textit{Contact time} + 9.825 \times \textit{Adsorbent dosage} + 31 \times \textit{Initial pH} - 0.061 \times \textit{Contact time} \times \textit{Adsorbent dosage} - 2.409 \times \textit{Contact time} \times \textit{Initial pH} - 9.149 \times \textit{Adsorbent dosage} \times \textit{Initial pH} + 0.013 \times \textit{Contact time} \times \textit{Adsorbent dosage} \times \textit{Initial pH} \quad (1)$$

This function describes how the experimental variables and their interactions influence the cupper adsorption. The initial pH of the solution had the greatest effect on removal (%), followed by adsorbent dosage, adsorbent dosage-initial pH interaction, contact time, contact time-initial pH interaction, contact time-adsorbent dosage interaction and contact time-adsorbent dosage-initial pH.

The positive values of these effects reveal that the increase of these parameters increased removal efficiency. Conversely, negative values of the effects decreased the response (removal %). Not only are the main effects modeled, but also their interactions, which is the main advantage of the 2^k factorial design compared to the traditional approach. This model was found to be adequate for prediction within the range of the chosen variables (Bingöl et al., 2010).

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 the respective mean-square-effect to the mean-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 100.00 % of removal efficiency variability. From the P-value, defined as the lowest level of significance leading to the rejection of the null hypothesis, it appears that the main effect of each factor and the interaction effects were statistically significant: $P<0.05$. The results revealed that the studied factors (contact time, adsorbent dosage and initial pH), their 2-way interaction (adsorbent dosage-initial pH interaction, contact time-initial pH interaction and contact time-adsorbent dosage interaction) and their 3-way interaction (contact time-adsorbent dosage-initial pH) were statistically significant to removal efficiency.

The main and the interaction effects

The main effects of the control factors upon adsorption process efficiency can be seen in Figure 1. In the Figure 1, it can be seen that the parameter contact time has a very weak positive effect upon responses. The adsorbent dosage has positive influence upon adsorption process efficiency. The initial pH has a strong positive effect upon responses.

Table 4 Estimated effects and coefficients for removal (%) (coded units).

Term	Effect	Coef	SE Coef	T	p
Constant		68.209	0.005229	13044.01	0.000
contact time	4.965	2.482	0.005229	474.74	0.000
adsorbent dosage	19.650	9.825	0.005229	1878.90	0.000
initial pH	62.000	31.000	0.005229	5928.33	0.000
contact time *adsorbent dosage	-0.122	-0.061	0.005229	-11.71	0.000
contact time (min)*initial pH	-4.817	-2.409	0.005229	-460.64	0.000
adsorbent dosage *initial pH	-18.298	-9.149	0.005229	-1749.58	0.000
contact time*adsorbent dosage*pH	0.025	0.013	0.005229	2.39	0.044

S = 0,0209165 R-Sq = 100,00% R-Sq(adj) = 100,00%

SE Coef: Standart Error Coefficient, Coef:Coefficient, *T*:Student's test value, ***p***: probability

Table 5 Analysis of variance for removal (%).

Source	DF	SS	MS	F	P
contact time	1	98.6	98.6	225382.63	0.000
adsorbent dosage(g/L)	1	1544.5	1544.5	3530262.86	0.000
initial pH	1	15376.0	15376.0	35145142.87	0.000
contact time* adsorbent dosage	1	0.1	0.1	137.20	0.000
contact time (min)*initial pH	1	92.8	92.8	212190.23	0.000
adsorbent dosage(g/L)*initial pH	1	1339.2	1339.2	3061014.92	0.000
contact time * adsorbent dosage*pH	1	0.0	0.0	5.71	0.044
Error	8	0.0	0.0		
Total	15	18451.2			

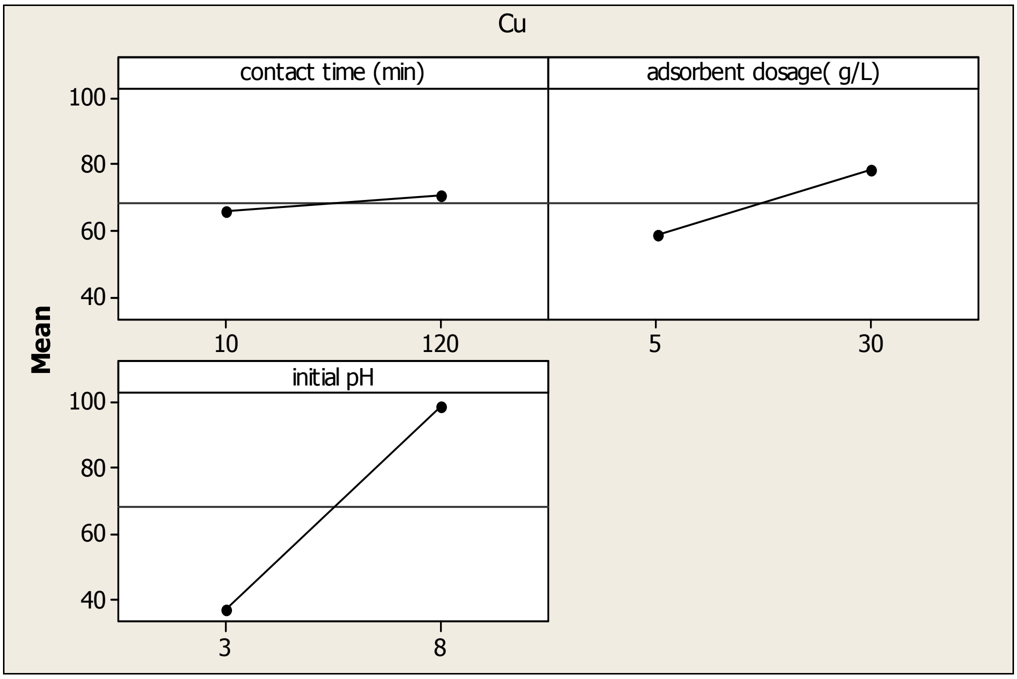

Fig. 1 Main effect plot for removal (%).

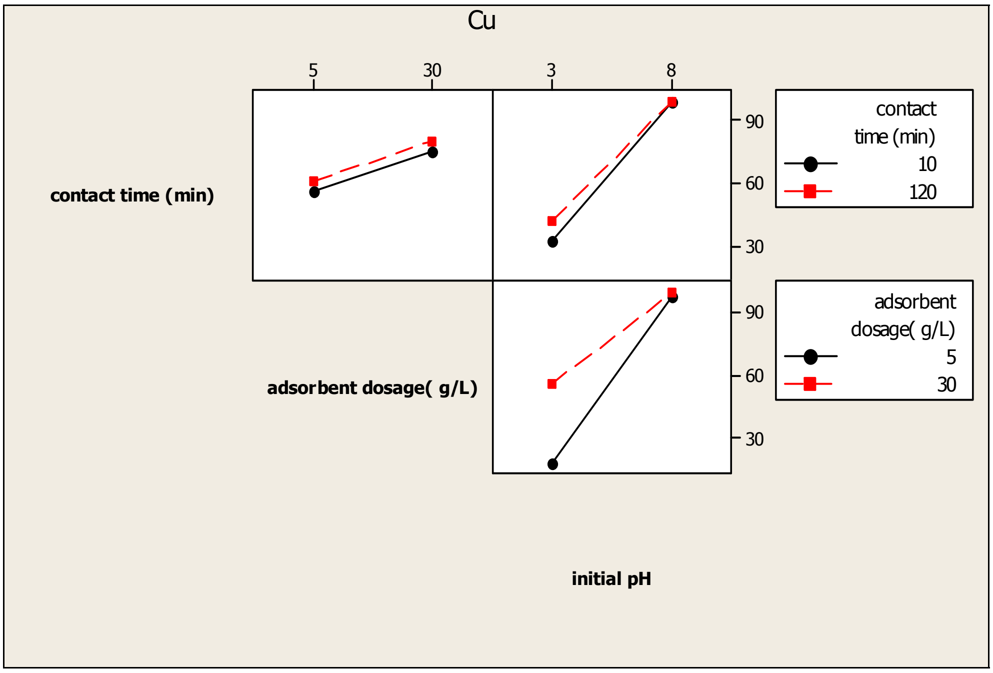

Fig. 2 Interaction effects plot for removal (%).

Increase in pH from 3 to 8 increaese the adsorption efficiency. Maximum adsorption occurred at basic pH. It is well known that pH of the aqueous solution is an important controlling parameter in the adsorption and ion exchange processes and metal removal typically increases with increasing pH values. Chemically, the solution pH influences metal speciation. For instance, heavy metal ions may form complexes with inorganic ligands such as OH^- (Çoruh, 2008; Argun, 2007; Malkoç, 2006).

These conclusions are in a strong correlation with the results obtained from the adsorption studies.

The interactions among different control factors for adsorption efficiency are presented in Figure 2. With exception of contact time all other interactions are when the lines in Figure 2, are not parallel. A strong deviation from the parallelism put in evidence a strong interaction among control factors. Figure 2 shows following significance interaction: contact time, adsorbent dosage and initial pH for adsorption efficiency, respectively. That means when will draw conclusion must be very carefully, because the interaction can mask the main effects of the control factors.

These screening designs have made a mathematical model, a linear one, for adsorption and efficiency. Adsorption results presented in present work are in good agreement with the adsorption studies found in literature. However, only the factorial design methodology can determine the most important principal and interactive factors to change the adsorption efficiencies at the solid/solution interface.

CONCLUSIONS

In this study, the removal of copper ions in the TCLP leachant using sepiolite was investigated by full factorial design approach. One factor at a time experiments were achieved, and the effects of initial pH, adsorbent dosage (g/L), contact time (min) were investigated on the removal efficiency.

The statistical design of the experiments combined with techniques of regression was applied in optimizing the conditions of maximum adsorption of the copper onto sepiolite. The main factors affecting the adsorption of copper were analyzed by using a full factorial design. The results obtained in this study show that the changes proposed in the factorial design study affected the removal efficiency of the copper ions by using sepiolite. The results of *ANOVA* indicated that the most considerable factor was initial pH for copper removal**.** The initial pH of the dispersion exerted the greatest influence on the amounts of copper adsorbed removal (%). Using sepiolite for copper removal, the best combination of the experimental variables that would give the maximum adsorption were ascertained: contact time 120 min, pH 8, and adsorbent dosage 30 g/L. To conclude, an integrated approach can provide a further contribution to develop a better understanding of adsorption process.

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