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Removal of lead from aqueous solutions by precipitation: statistical analysis and modeling

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ABSTRACT

Chemical precipitation is the most common technology for the removal of dissolved metals from industrial wastewater. In this study, the removal of Pb(II) from aqueous solutions by precipitation was investigated and factorial design was applied. The effects of three variables i.e. pH, mass of precipitating agent, and precipitation time on the removal of lead were evaluated. The significance of the effects was checked by analysis of variance within a 95% confidence level. The model function equation for lead removal was obtained. Analysis of variance, *t*-test, and *F*-test showed that the precipitation time (*C*) had the greatest effect on Pb(II) removal, followed by mass of precipitating agent (*B*), pH (*A*), mass of precipitating agent–precipitation time (*BC*), and pH–precipitation time (*AC*). The maximum Pb(II) removal efficiency obtained at the optimum conditions was 99.42%. The removal of Pb(II) from industrial effluent was also studied.

Keywords: Lead; Heavy metal removal; Chemical precipitation; Factorial design

1. Introduction

As a result of rapid industrialization, toxic metals and metalloids such as cadmium, lead, chromium, mercury, arsenic, and copper are released into the environment resulting in damage in ecosystems and human health. Hence, the presence of heavy metals in natural or industrial wastewaters is a subject of great interest as one of the most serious worldwide environmental problems in environmental science. Among the different heavy metals, lead is one of the common and most toxic pollutants released into the natural waters from various industrial activities such as metal plating, oil refining, and battery manufacturing. Lead ions are taken into body via inhalation, ingestion, or skin adsorption [1]. In drinking water maximum allowable limit of total Pb of 50 μg/L is considered safe by the World Health Organization [2], whereas less than 15 μg/L is adopted by the United States Environmental Protection Agency [3]. Due to toxic effects of lead and other toxic metal ions, the removal of them from waters and wastewaters is important in terms of protection of public health and environment.

The traditional methods, for the treatment of lead and other toxic heavy metal contaminated wastewaters, include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation, and coagulation.

Precipitation processes could be directly used for the treatment of aqueous solutions containing toxic

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metals. Some of the most common inorganic pollutants (such as heavy metals) can be treated in this way. For this purpose, numerous additives forming rather insoluble solid phases can be used. The most important among them are the hydroxides of alkali and alkali earth metals, such as NaOH, KOH, $Ca(OH)_2$, sulfides, phosphates, and carbonates [4]. The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost, and ease of pH control [5,6]. The solubilities of the various metal hydroxides are minimized in the pH range of 8.0–11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides have been used to precipitate metals from wastewater, based on the low cost and ease of handling; lime is the preferred choice of base used in hydroxide precipitation at industrial settings.

A comparison of the precipitation removal efficiency 99.42% observed in this study with other precipitation removal efficiencies in the literature is given in Table 1.

The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. (1):

$$M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2 \downarrow \tag{1}$$

where M^{2+} and OH^{-} represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide [13].

Hydroxide precipitation process using $Ca(OH)_2$ and NaOH in removing Cu(II) and Cr(VI) ions from wastewater was evaluated by Mirbagheri and Hosseini [14]. The Cr(VI) was converted to Cr(III) using ferrous sulfate. Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of $Ca(OH)_2$ and the chromate concentration was reduced from 30 to 0.01 mg/L. The cuproammonia was reduced by aeration and the optimum pH for maximum copper precipitation was about 12 for both $Ca(OH)_2$ and NaOH and the concentration of copper was reduced from 48.51 to 0.694 mg/L. To enhance lime precipitation, fly ash was used as a seed material [8]. The fly ash–lime carbonation treatment increased the particle size of the precipitate and significantly improved the efficiency of heavy metal removal. The concentrations of chromium, copper, lead, and zinc in effluents can be reduced from initial concentrations of 100 to 0.08, 0.14, 0.03, and 0.45 mg/L, respectively.

Chemical precipitation has been shown to be successful in combination with the other method. González-Muñoz et al. [15] reported sulfide precipitation to reuse and recover heavy metal ions and they employed nanofiltration as a second step. The results indicated that sulfide precipitation was successful in reducing the metal content and the nanofiltration yielded solutions could be directly reused in the plant. Ghosh et al. [7] used electro-Fenton process and chemical precipitation to treat rayon industry wastewater to reduce its Chemical Oxygen Demand (COD) (2,400 mg/L) and Zn^{2+} (32 mg/L). The results revealed that approximately 88% COD was reduced using electro-Fenton method and zinc removal (99–99.3%) was attained in the range of pH 9–10 using

Table 1
Removal efficiency (%) of various precipitants as reported in literature

Species	Initial metal conc.	Precipitant	Optimum pH	Removal efficiency (%)	Ref.
Zn^{2+}	32 mg/L	CaO	9–10	99–99.3	[7]
Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}	100 mg/L	CaO	7–11	99.37–99.6	[8]
Cu^{2+}, Zn^{2+}, Pb^{2+}	0.018, 1.34, 2,3 mM	H_2S	3.0	100 > 94 > 92	[9]
Cr^{3+}	5,363 mg/L	CaO and MgO	8.0	>99	[10]
Hg^{2+}	65.6, 188 μg/L	1,3-benzenediamidoethanethiolate	4.7 and 6.4	>99.9	[11]
CuEDTA	25, 50, 100 mg/L	1,3,5-hexahydotriazinedithiocarbamate	3.0	99.0, 99.3, 99.6	[12]
Pb^{2+}	100 mg/L	$Ca(OH)_2$	12	99.42	This study

lime precipitation. There are some reports on chemical precipitation in combination with ion exchange treatments. Papadopoulos et al. [16] reported the use of ion exchange processes individually and then combining with chemical precipitation in removing nickel from wastewater streams from a rinse bath of aluminum parts. They found that the individual application of ion exchange led to the removal of nickel up to 74.8%, while using the combination of ion exchange and precipitation processes, a higher removal from 94.2 to 98.3% was obtained. Besides, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange, was also reported [17].

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response [18]. The advantages of factorial experiments include the relatively low cost, a reduced number of experiments, and increased possibilities to evaluate interactions among the variables. The most popular first-order design is the two-level full factorial, in which each factor is experimentally studied at only two levels that are expressed in coded form: −1 for low level and +1 for high level. The full factorial design consists of a 2^k experiments (k factors, each experiment at two levels), which are very useful for either preliminary studies or in initial optimization steps, while fractional designs are almost mandatory when the problem involves a large number of factors [19].

In the present work, the removal of lead from aqueous solutions by precipitation was investigated. A 2^3 full factorial design was used to evaluate the importance of pH, mass of precipitating agent, and precipitation time.

2. Materials and methods

2.1. Solution preparation and reagents

The stock solution of Pb(II) (1,000 mg/L) was prepared by dissolving 1.5985 g of analytical grade $Pb(NO_3)_2$ in 1,000 mL of double distilled water such that each mL of the solution contains 1 mg of divalent lead. The required lower concentration (100 mg/L) was prepared by dilution of the stock solution which was prepared freshly for each experiment. The calcium oxide used was of 98% purity (Aldrich Chemical Co.).

2.2. Scanning electron microscopy analysis

The surface of $Ca(OH)_2$ was also characterized by scanning electron microscopy (SEM) (JEOL-JSM-5600 LV) before and after the precipitation experiments. Samples were gold–palladium coated prior to SEM observation. Images were collected with a beam potential of 20 kV.

2.3. Precipitation

The precipitation of lead from the solutions involved batch experiments at room temperature (20 ± 1°C) in sealed 500 mL polyethylene vessels. $Ca(OH)_2$ was added at a desired amount to 200 mL of the heavy metal solutions. After the addition of $Ca(OH)_2$, the suspensions were agitated at 200 rpm for 3 min using a magnetic stirrer, followed by gentle stirring at 40 rpm for 10 and 30 min to promote precipitation. The pH measurements were carried out with a pH meter (Thermo). After mixing, the suspensions were allowed to settle for 30 min, and the supernatant (20 mL) from each vessel was collected and acidified to <pH 2 by adding nitric acid, filtered through 0.45 mm Whatman filters and they were analyzed by atomic absorption spectrophotometer (Perkin Elmer, Analyst A400).

2.4. The factorial design

The high and low levels defined for the 2^3 factorial design are listed in Table 2. The low and high levels for the factors were selected according to some preliminary experiments. The factorial design matrix and removal efficiency (%) in each factorial experiment is shown in Table 3.

2.5. Removal of lead from industrial effluent

The effluent containing lead (10 mg/L) was collected from an industrial electroplating process plant located in Eskişehir, Turkey and the precipitation experiment was carried out at optimum conditions using the effluent as feed solution.

Table 2
Independent variables and their levels used for 2^3 factorial design

Variables	Symbol	Range and levels	
		Low level (−1)	High level (+1)
pH	*A*	8	12
Mass of precipitating agent (g/L)	*B*	0.25	0.75
Precipitation time (min)	*C*	10	30

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

Experiment	*A*	*B*	*C*	Removal (*R*%)
1	−1	−1	−1	84.26
2	+1	−1	−1	87.29
3	−1	+1	−1	90.15
4	+1	+1	−1	93.33
5	−1	−1	+1	94.20
6	+1	−1	+1	95.82
7	−1	+1	+1	97.56
8	+1	+1	+1	99.50

3. Results and discussion

3.1. Experimental design

The results were analyzed with the Minitab 16 software, and the main effects and interactions between the factors were determined. The codified model employed for the 2^3 factorial design is described in Eq. (2).

$$R\ \% = \beta_0 + \beta_1 X_{1i} + \beta_2 X_{2i} + \beta_3 X_{3i} + \beta_{12} X_{1i} X_{2i} + \beta_{13} X_{1i} X_{3i} + \beta_{23} X_{2i} X_{3i} + \beta_{123} X_{1i} X_{2i} X_{3i} \qquad (2)$$

where $R\%$ is the predicted response; X_{ji} values ($j = 1, 2, 3;\ i = 1, 2, 3, \ldots, 8$) indicate the corresponding parameters in their coded forms; β_0 is the average value of the result; and β_1, β_2, and β_3 are the linear coefficients. For Pb(II) precipitation, the coefficients β_1, β_2, and β_3 indicate the effect of pH (*A*), mass of precipitating agent (*B*), and precipitation time (*C*), respectively. Coefficients β_{12}, β_{13}, and β_{23}, respectively, describe the interacting effects of pH–mass of precipitating agent, pH–precipitation time, and mass of precipitating agent–precipitation time. Coefficient β_{123} implies the interacting effect of pH-precipitating agent–precipitation time.

Substituting the regression coefficients in Eq. (3), we get a model equation relating to the level of parameters and Pb(II) precipitation efficiency:

$$R\% = 92.7638 + 1.2212\ A + 2.3712\ B + 4.0062\ C + 0.0588\ AB - 0.3313\ AC - 0.6112\ BC + 0.0213\ ABC \qquad (3)$$

The reduced model which includes the effects determined to be “significant” can be expressed as:

$$R\% = 92.7638 + 1.2212\ A + 2.3712\ B + 4.0062\ C - 0.3313\ AC - 0.6112\ BC \qquad (4)$$

This function describes how the experimental variables and their interactions influence the lead precipitation. The precipitation time (*C*) had the greatest effect on *R*(%), followed by mass of precipitating agent (*B*), pH (*A*), mass of precipitating agent–precipitation time (*BC*), and pH–precipitation time (*AC*). The positive values of these effects reveal that the increase of these parameters increased *R*%. Conversely, negative values of the effects decreased the response (*R*%). According to Eq. (4), the pH (*A*), mass of precipitating agent (*B*), and precipitation time (*C*) had a positive effect on (*R*%), while pH–precipitation time (AC) and mass of precipitating agent–precipitation time (*BC*) had a negative effect.

In order to ensure an appropriate model, the test for the significance of regression was performed by applying a variance analysis (ANOVA). According to the ANOVA table (Table 4), $p < 0.05$ for the main factors and their two-way interactions, and the R^2 value for *R*% was 99.94%. Also, the predicted R^2 value was in agreement with the adjusted coefficient of determination, R^2 (adj). The three studied variables must be manipulated at the highest level of pH, mass of precipitating agent, and precipitation time (+, +, +).

Table 5 shows the sum of squares being used to estimate the factors' effect and the *F*-ratios, which are

Table 4
Estimated effects and coefficients for Pb(II) removal

Term	Effect	Coeff.	SE Coeff.	*t*	*p*
Constant		92.7638	0.04418	2,099.84	0.000
A	2.4425	1.2212	0.04418	27.64	0.001
B	4.7425	2.3712	0.04418	53.68	0.000
C	8.0125	4.0062	0.04418	90.69	0.000
AC	−0.6625	−0.3313	0.04418	−7.50	0.017
BC	−1.2225	−0.6112	0.04418	−13.84	0.005

Note: $S = 0.124{,}950$, *R*-Sq (pred.) = 99.74%, *R*-Sq (adj.) = 99.94%.

Table 5
Analysis of variance for Pb(II) removal

Source	DF	Seq. SS	Adj. SS	Adj. MS	*F*	*p*
A	1	11.392	11.932	11.932	764.23	0.001
B	1	44.983	44.983	44.983	2,881.19	0.000
C	1	128.400	128.400	128.400	8,224.20	0.000
AC	1	0.878	0.878	0.878	56.22	0.017
BC	1	2.989	2.989	2.989	191.45	0.005
Residual error	2	0.031	0.031	0.016		
Total	7	189.213				

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 statistics indicated that the first-order model gave 99.94% of *R*%'s variability. 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 (*A*, *B*, *C*) and their two-way interaction (*AC* and *BC*) were statistically significant to *R*%. Notably, three-way interaction (*ABC*) had no effect at the 95% confidence level.

Fig. 1 shows the Pareto chart, which gives the relative importance of the individual and interaction effects. The vertical line in the chart indicates the minimum statistically significant effect magnitude at the 95% confidence level. Since any effect that extends the reference line is potentially important, the main effects of *C*, *B*, *A*, and *BC* and *AC* interaction are important parameters in the response variable.

The main effect plots were used to visualize which factors affect the response most significantly (Fig. 2). Each level of the factors affected the precipitation efficiency in a different way. For Pb(II) ions, high levels of *A*, *B*, and *C* resulted in higher mean responses compared to the low levels. The factor *C* had the greatest effect as indicated by the steep slope as seen in Fig. 2.

If there were no significant interactions between the factors, a main effects plot would adequately describe the changes [20]. In general, the interaction plot describes the impact of changing the settings of one factor on another factor. The interactions plots of pH–*t* and *m*–*t* are depicted in Figs. 3 and 4, respectively.

According to Fig. 3, the pH–*t* interaction indicates that precipitation time (*t*) has little effect at low pH but a large positive effect at high pH. Therefore, higher percentage of Pb(II) removal would appear to be obtained when pH and *t* are at the high levels (pH = 12 and *t* = 30 min, respectively). Similarly, in Fig. 4, the *m*–*t* interaction indicates that precipitation time (*t*) has little effect at low mass of precipitating agent (*m*) but a large positive effect at high mass of precipitating agent (*m*). Therefore, higher percentage

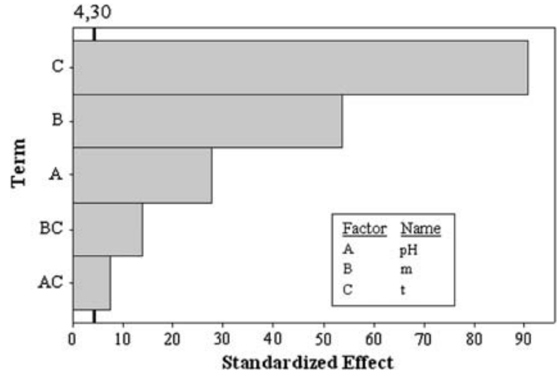

Fig. 1. Pareto chart of the standardized effects.

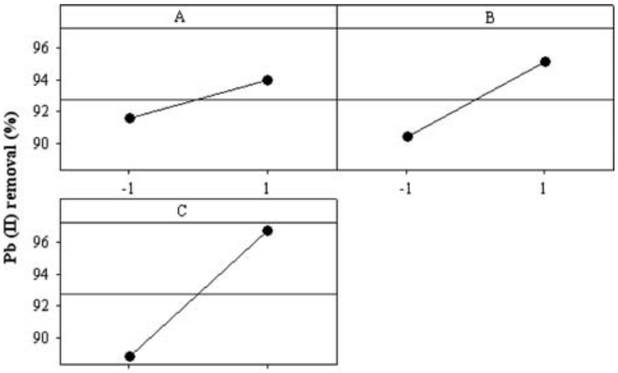

Fig. 2. Main effects plot for Pb(II) removal (%).

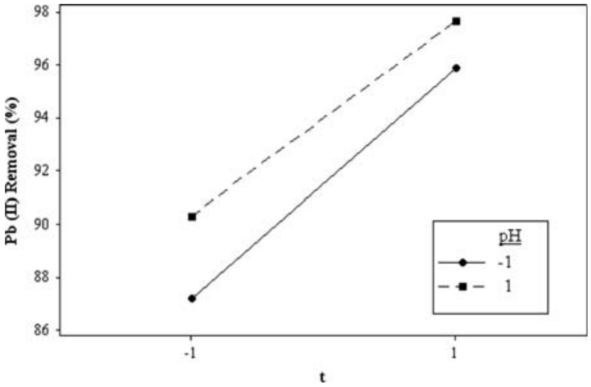

Fig. 3. Effect plot for pH and *t* interaction.

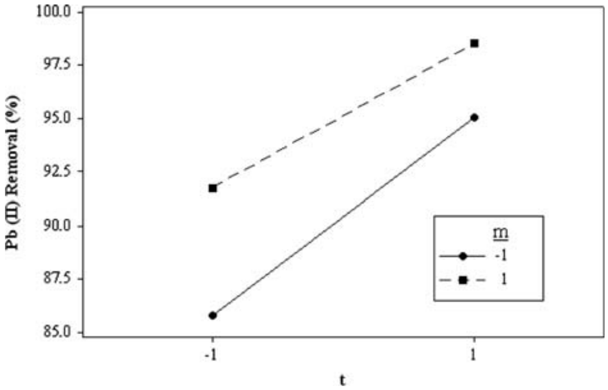

Fig. 4. Effect plot for *m* and *t* interaction.

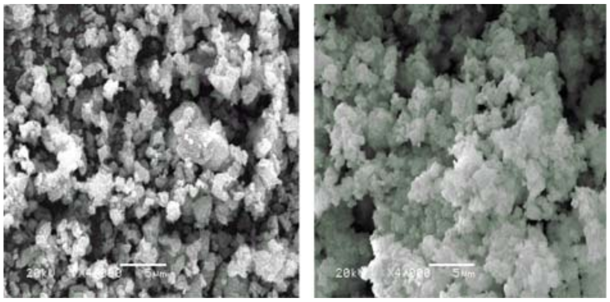

Fig. 5. SEM micrographs of $Ca(OH)_2$ (a) before and (b) after Pb(II) precipitation.

of Pb(II) removal would appear to be obtained when m and t are at the high levels ($m = 0.75$ g/L and $t = 30$ min, respectively).

3.2. SEM analysis of the resin

For comparison, $Ca(OH)_2$ samples before and after the precipitation of lead ions were analyzed for their surface appearance. The SEM micrographs are shown in Fig. 5(a) and (b). It is found that before precipitation, the $Ca(OH)_2$ material was composed of irregularly shaped particles, and large flake-like species were formed on the surface of the $Ca(OH)_2$ after the precipitation of Pb(II).

3.3. Removal of lead from industrial effluent

In order to investigate the feasibility of lead removal, the industrial effluent containing lead (10 mg/L) from electroplating was treated. The precipitation experiment was carried out at optimum conditions (pH = 12; mass of precipitating agent = 0.75 g/L and precipitation time = 30 min). A very high lead removal of 99.5% was reached.

4. Conclusions

The precipitation of lead ions with $Ca(OH)_2$ was carried out to reduce the level of lead concentration in the solution. In order to determine the effects of various operating conditions (pH, mass of precipitating agent, and precipitation time) and their interactions on the precipitation of Pb(II) ions, a full 2^3 factorial design was performed. Analysis of variance (ANOVA), t-test, and F-test showed that the precipitation time (C) had the greatest effect on $R(\%)$, followed by mass of precipitating agent (B), pH (A), mass of precipitating agent–precipitation time (BC), and pH–precipitation time (AC). The maximum Pb(II) removal efficiency obtained at the optimum conditions was 99.42% which means an almost complete removal.

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