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F. GÜNAYDIN, A. ÖZER, H.S. ALTUNDOGAN, M. ERDEM AND F. TÜMEN*

Firat University, Department of Chemical Engineering, 23279, ELAZIG-TURKEY

ABSTRACT

This study deals with the removal of Cr(VI) from aqueous solutions by using filter cake known as zinc extraction residue (ZER) generated as a by product in a zinc production plant located in Kayseri-TURKEY. It was found that ZER, which is rich in lead compounds, has a great affinity for chromate ions. The Cr(VI) removal yield decreased with increasing initial concentration of Cr(VI) solution. An increase in the dosage of ZER caused an increase in the removal yield and the concentration of Pb, Cd and Zn released from ZER into the treated solution. The effect of temperature showed the removal process is endothermic. The removal process was highly pH dependent. 100 % removal of Cr(VI) was obtained at initial pH about 5.0 and 11.0 for the initial Cr(VI) concentration of 100 mg l^{-1} at 25 °C and 5 mg l^{-1} ZER dosage for contact time of 60 min. The removal percentage of Cr(VI) declined at pHs other than those mentioned above. Minimum removal (26.5 %) was observed at initial pH value of 3.05. XRD analysis showed that low-solubility lead chromates were formed in the removal process.

INTRODUCTION

Chromium is one of the most toxic heavy metals introduced into natural waters from chrome tanning, aluminium anodising, paint pigment production and metal cleaning and electroplating operations [1]. Chromium occurs in aqueous systems as both Cr(III) and Cr(VI) forms. The wastewaters from the processes mentioned above contain Cr(III) and Cr(VI) at various levels. The Cr(VI) is more toxic than Cr(III), hence, it is of particular concern. It is found as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions in aqueous systems. The various forms of Cr(VI) can be converted to each other by changing the pH of the medium [2]. The most common method of Cr(VI) removal consists of two stages: reduction of Cr(VI) to Cr(III) and subsequent precipitation of Cr(III) [1,3,4]. In practice, the reduction of Cr(VI) is carried out by using reductants such as sulphur dioxide, sodium bisulphite, sodium metabisulphite or ferrous sulphate in a strong acidic medium. The precipitation of Cr(VI) in waste waters without reduction would decrease the cost of the removal process, to a large extent. The Cr(VI) can be directly precipitated in the form of insoluble chromate salts. Lead nitrate [5] and barium carbonate [6] have been used to precipitate the Cr(VI) directly from aqueous solutions. However the use of these salts for precipitation of Cr(VI) is not feasible economically, since such manufactured materials have high costs. In the zinc production process, more than 100 tons zinc extraction

residue (ZER) is generated daily as a by product. Because of the high lead content of the residue, it is dumped in open stockpiles and retained for lead recovery in the future. This waste with readily fine particles has no cost except for transportation expenditures. In a previous study [7] dealing with the solubility of ZER, known as lead-filter cake, it was found that this residue released a significant amount of lead ions into the water. The lead ions solubilised from ZER give a precipitate with chromate ions in aqueous solutions, therefore, the use of ZER as a precipitant for chromate ions is more suitable than manufactured salts such as lead nitrate and barium carbonate.

In this study, the direct removal of Cr(VI) from aqueous solutions was examined by using zinc extraction residue (ZER) which contains lead compounds. Chromate solutions having different concentrations were treated with various amount of ZER by using a batch system, and the influence of various parameters affecting the removal yield were investigated. In addition, the concentration of some metals solubilised from ZER was determined throughout the study.

MATERIALS AND METHODS

Material

Zinc extraction residue (ZER) used in this study is

formed during the leaching of calcined carbonate ores with sulphuric acid to obtain electrolyte for zinc production. This material was provided from a zinc plant located in Kayseri-Turkey. ZER samples obtained in the form of powder were dried to remove the humidity, and sieved to obtain -200 mesh fraction. To remove excess acid, 500 g of ZER was washed with 2.5 l of deionized water by shaking the suspension in a polyethylene bottle of 5 l capacity at 80 cycle min⁻¹. The supernatant was removed by suction at the end of 60 min. The residue obtained at the final stage was dried at 105 °C and sieved. The fraction of -200 mesh were used in all experiments. The dissolution of ZER was carried out by utilising the lithium metaborate fusion-nitric acid dissolution method [8] and its chemical composition was determined by an atomic absorption spectrophotometer (Perkin Elmer 370).

Preparation of solutions

A stock solution of Cr(VI) (10 000 mg l⁻¹) was prepared by dissolving K_2CrO_4 (%99, Riedel 1224) in distilled water. All working solutions were prepared by diluting stock solution with distilled water. HNO_3 and NaOH, used for adjusting pH of solutions, were of analytical grade.

Experimental procedure

Cr(VI) removal experiments were carried out by contacting ZER with Cr(VI) solution in a continuously mixed batch system. All experiments were performed with a 100 ml Cr(VI) solution in 150 ml flasks using a flask shaker (Stuart Scientific, SF1 model) equipped with a temperature controlled-water bath.

In the first section of the study, the effect of contact time and the initial concentration of Cr(VI) solution on the removal of Cr(VI) were investigated. Solutions with different initial Cr(VI) concentrations were treated with 0.5 g ZER at 25 °C for a contact period varying from 5 to 240 min.

The effect of ZER dosage was investigated by treating Cr(VI) solution (100 mg l⁻¹) with ZER at doses ranging from 5 to 100 g l⁻¹ for different contact periods.

In the experiments where the effect of temperature was examined, ZER dosage and the initial concentration of Cr(VI) solutions were selected as 5 g l⁻¹ and 100 mg l⁻¹, respectively. These experiments were carried out at different temperatures (40, 55 and 70 °C) using contact times varying from 5 to 240 min.

To study the effect of pH, the initial pH of Cr(VI) solutions (100 mg l⁻¹) was varied from 3.0 to 13.5 and the solution were contacted with 5 g ZER samples for a period of 60 min at 25 °C.

In all the experiments, at the end of the predetermined contact time, the reaction mixtures were filtered to separate supernatant and residue. After filtration, the pHs of supernatants were measured and recorded as final pH.

Methods of analysis

The analysis of Cr(VI) in the supernatants was carried out colorimetrically with 1,5 diphenyl carbazide method [9] by spectrophotometer (Bausch & Lomb, Spectronic 20). The uptake of Cr(VI) was calculated by differences between the initial and final concentration of solution. The concentrations of Pb, Cd and Zn solubilised from ZER were determined using a Perkin Elmer 370 model flame atomic absorption spectrophotometer. Except for these metals, the amount of the other metals in treated solution were not determined since they show the less solubilisation.

RESULTS AND DISCUSSION

The composition of ZER

The chemical composition of the zinc extraction residue (ZER) used in this study is given in Table 1. The main constituents of ZER are lead, zinc and iron. In addition to these metals, it contains cadmium, nickel, cobalt, copper and manganese in trace amounts. X-ray diffraction analysis shows that the ZER contains anglesite ($PbSO_4$), maghemite (Fe_2O_3) and gypsum ($CaSO_4$ $2H_2O$).

The effect of initial concentration and contact time

The influence of the initial concentration of chromate solution on the removal efficiency and the variation of concentrations of Pb, Zn and Cd ions solubilised from ZER with contact time are given in Figure 1. As seen from the Figure, 100 % removal of chromate ions in 100 ml solution with a concentration of 50 mg l⁻¹ was achieved using 0.5 g ZER within a contact time of 45 min, and for a solution of 100 mg l⁻¹ this was achieved in 240 min. With increasing initial concentration above 100 mg l⁻¹, the time required for the removal of all chromate ions increased. On the other hand, the concentration of lead in the mixture began to increase from the point at which the chromate ions were fully removed. Thus, the removal of chromate ions is directly dependent on the presence of lead ions and at higher chromate concentrations, the amount of solubilised lead ions is not sufficient to remove the chromate ions completely. This suggests that the removal mechanism is based on the

Table 1.   The chemical composition of zinc extraction residue.

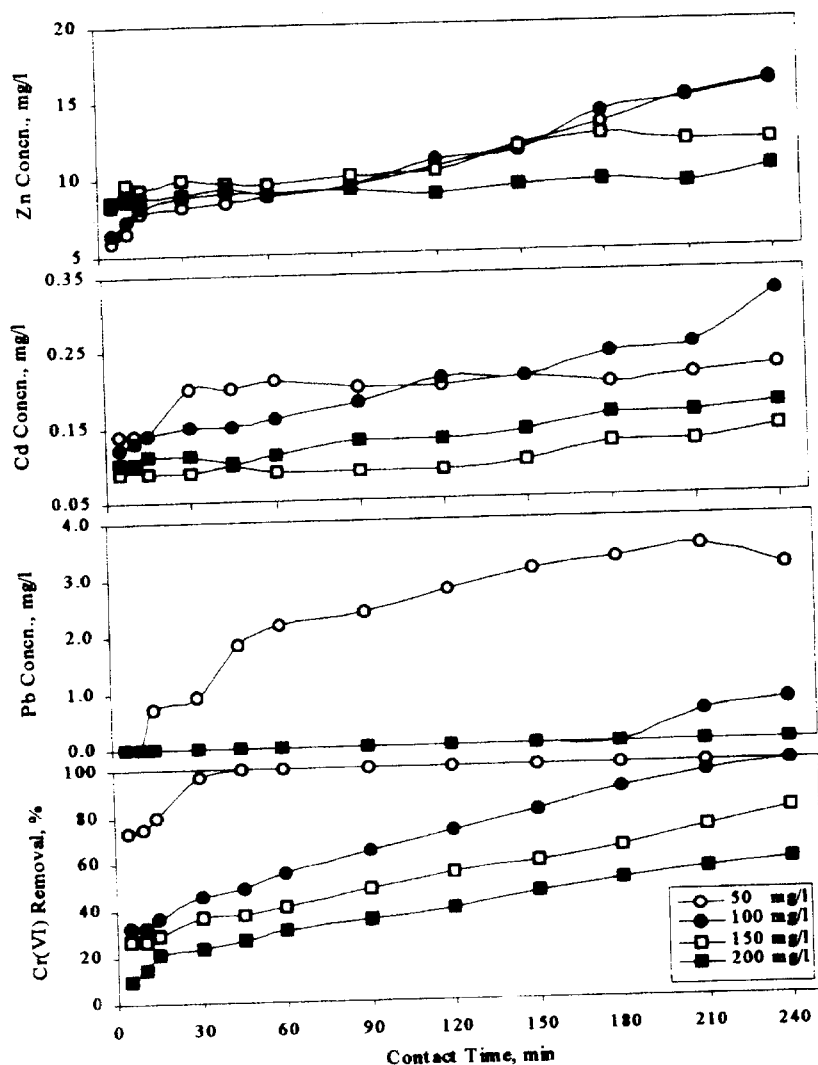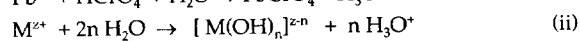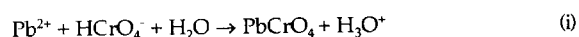| Constituent	Pb	Zn	Fe	Cd	Ni	Co	Cu	Mn
	%	%	%	(mg kg⁻¹)	(mg kg⁻¹)	(mg kg⁻¹)	(mg kg⁻¹)	(mg kg⁻¹)
Composition	28.10	9.06	7.11	550	300	240	2000	2900

Figure 1. Effect of initial concentration of solution on the removal of Cr(VI) and variation of concentration of solubilised metals with contact time (Conditions: ZER dosage: 5 g l^{-1}; temperature: 25 °C; pH: not adjusted).

precipitation of chromate ions as PbCrO$_4$ and/or the adsorption of chromate ions on the ZER surface. The concentration of cadmium determined in the treated solutions are quite low compared to those of lead and zinc. But cadmium is of particular importance due to its toxicity and its concentration is restricted at 0.01 mg l^{-1} by various quality standards developed for surface water [10]. The maximum concentration of cadmium for drinking water is given 0.005 mg l^{-1} [11]. As seen, the cadmium concentration is higher than this limit. However, cadmium ions may be precipitated as hydroxide by adjusting pH of the treated solution. Zinc is the most solubilised metal from ZER and its concentration increased to 15.8 mg l^{-1}. However, zinc concentrations in the treated solutions decreased with increasing initial concentration of chromate. In addition, in

the final pH of mixtures showed a decreasing trend with increasing contact time, and this decline is more noticeable under conditions where chromate ions are not detected. The decrease in the values of final pH may be attributed to the formation PbCrO$_4$ and hydrolysis of metal ions in aqueous solution as following.

$$Pb^{2+} + HCrO_4^- + H_2O \rightarrow PbCrO_4 + H_3O^+ \qquad (i)$$
$$M^{z+} + 2n\,H_2O \rightarrow [\,M(OH)_n\,]^{z-n} + n\,H_3O^+ \qquad (ii)$$

Where letter M represents the metal ions.

The effect of ZER dosage

The effect of ZER dosage on the removal process was

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studied for an initial Cr(VI) concentration of 100 mg l^{-1} by varying ZER dosage from 5 to 20 g l^{-1} and using different contact times. The obtained results are shown in Figure 2. The removal efficiency of chromate increased with the dosage of ZER and contact time. For example, the time required for the complete removal of Cr(VI) in the solution of 100 mg l^{-1} by using 5 g l^{-1} ZER dosage is 240 min. However, when two times ZER dosage was used at the same conditions, all chromate ions in the solution were removed within 90 min. Thus, the higher the ZER dosage, the less contact time is needed. As expected, the amount of solubilised lead from ZER increased with increase in ZER dosage. The maximum concentration of lead ions was determined as about 0.70 mg l^{-1} at a dosage of 5 g l^{-1}. For the dosages of 7.5, 10, 15 and 20 g l^{-1}, the maximum concentrations of lead are 1.36, 2.00, 2.55 and 3.00 mg l^{-1}, respectively. These values are over the toxicity

limits given for lead [10,11]. But the magnitude of lead concentration depends on, to a large extent, the amount of chromate ions remaining in the solution. The concentration of chromate ions varied with both ZER dosage and contact time, hence, both parameters must be optimized to prevent the passing of lead ions to the solution. The solubilisation of cadmium and zinc is also dependent on the ZER dosage and contact time. Significant amounts of these metals were detected to be solubilised in the first 30 min of contact period. In all cases, the concentration of cadmium is lower compared to zinc concentration.

Effect of temperature

Figure 3 shows the results of experiments carried out at 25, 40, 55 and 70 °C. The data presented in the Figure were
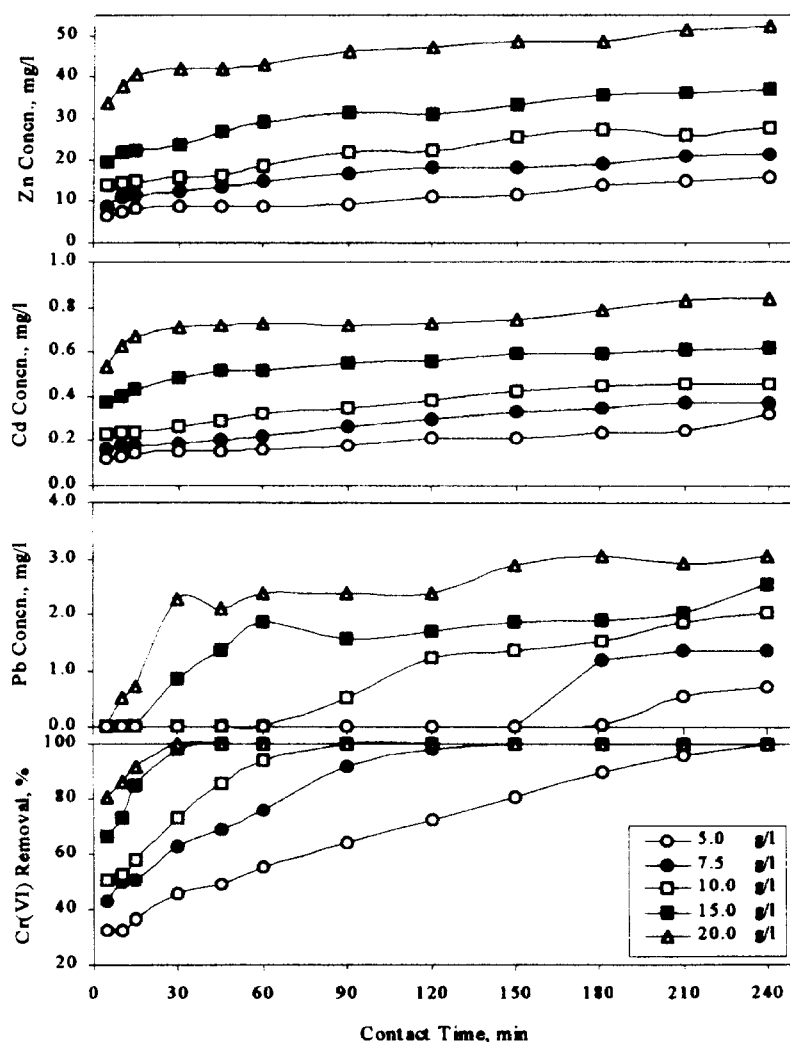

Figure 2. Effect of ZER dosage on the removal of Cr(VI) and change of concentration of solubilised metals with contact time (Conditions: initial concentration of solution: 100 mg Cr(VI) l^{-1}; temperature: 25 °C; pH: not adjusted).
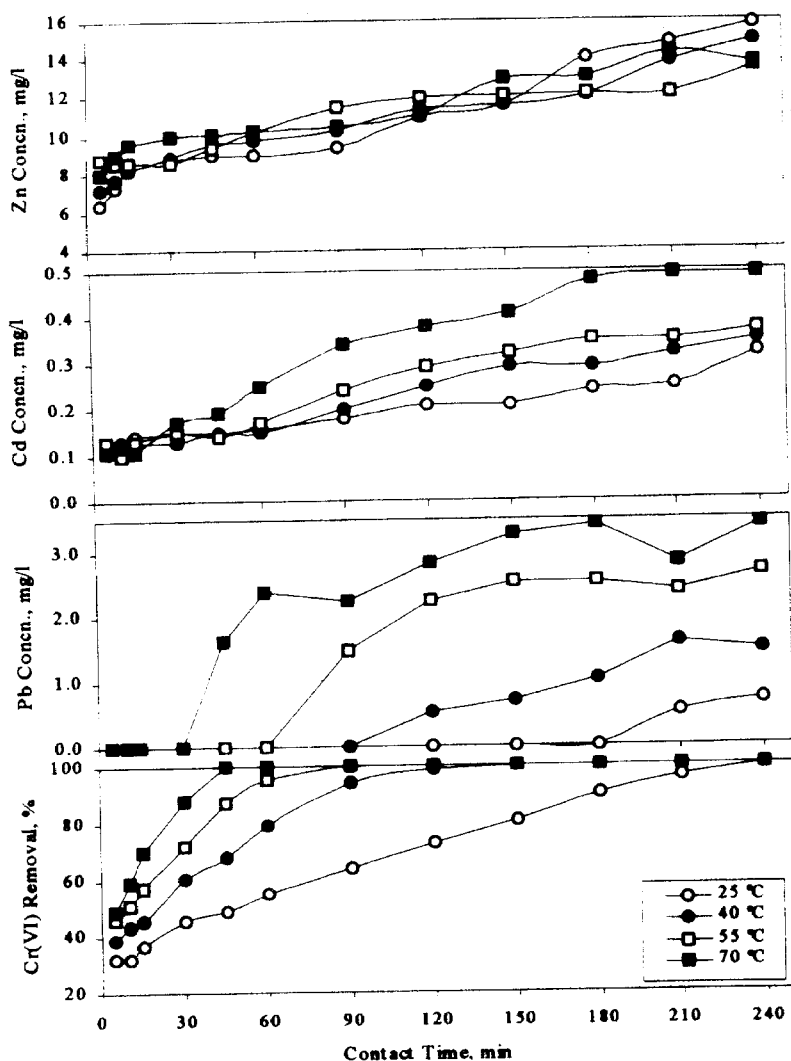
Figure 3. Effect of solution temperature on the removal of Cr(VI) and change of concentration of solubilised metals with contact time (Conditions: initial concentration of solution: 100 mg Cr(VI)l⁻¹; ZER dosage: 5 g l⁻¹; pH: not adjusted).

obtained by contacting the solution (100 mg Cr(VI) l⁻¹) with ZER at 5 g l⁻¹ dosage. It can be seen that the temperature of the solution has a positive effect on the removal of Cr(VI). At the end of the contact period of 45 min, the removal percentages of Cr(VI) were found to be 49.0, 67.9, 87.5 and 100 at the solution temperatures of 25, 40, 55 and 70 °C, respectively. However, when the contact time was increased up to 240 min the Cr(VI) in the solution may also be removed completely at lower temperatures. The variation of Cr(VI) removal yield with temperature indicated that this process was endothermic. The concentrations of solubilised metals, except for zinc, show increasing trends with temperature of solution. This situation may be disadvantageous due to the toxic characteristic of these metals. Moreover, high temperature is one of most important factors affecting the cost of process.

Effect of pH

The results relating to the effect of pH are given in Figure 4. In this section of the study, 100 ml of 100 mg l⁻¹ Cr(VI) solution was treated with 0.5 g ZER at different pH values for a contact time of 60 min. Since the surface charges of a solid treated with an aqueous solution may be modified by changing the pH the of medium, it is expected that the pH of the solution is one of the most important parameters affecting the yield of such processes. It is obvious that the removal efficiency of Cr(VI) and the concentration of metal ions released from ZER are highly pH dependent. The initial pHs of solutions contacted with ZER are different from the final pHs.
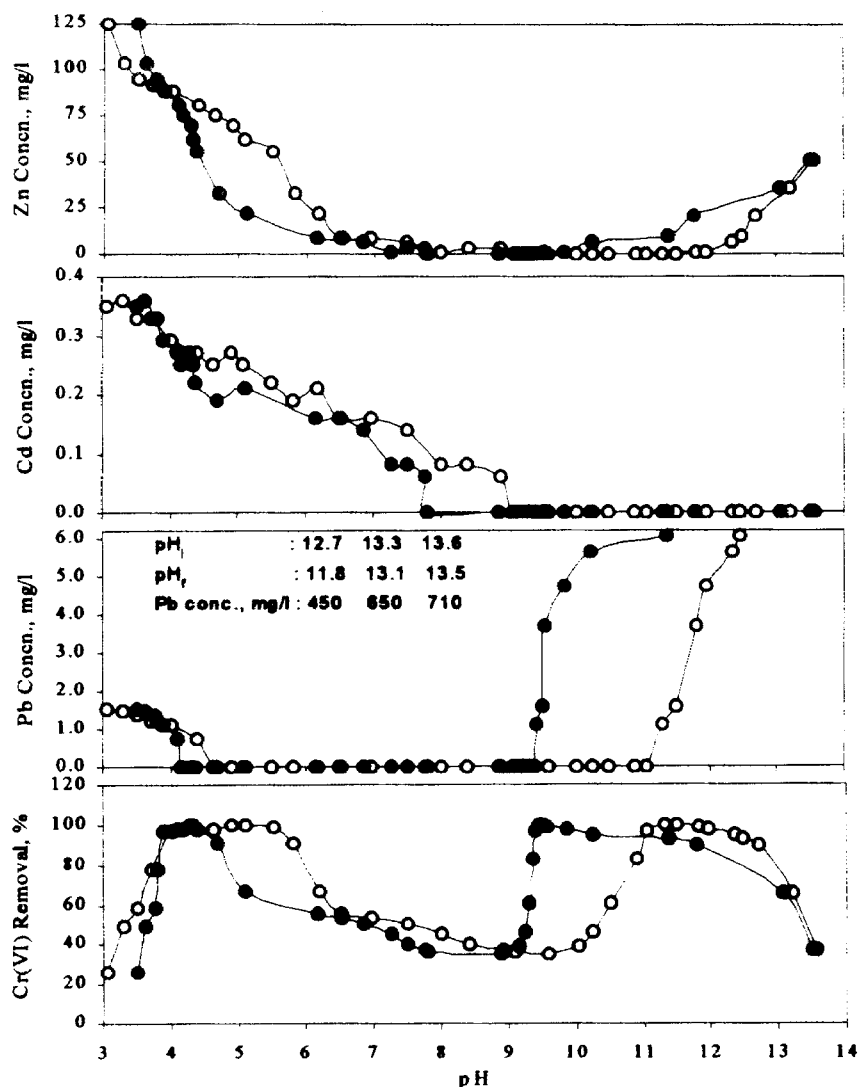
Figure 4. Effect of pH on the removal of Cr(VI) and change of concentration of solubilised metals with contact time (Conditions: initial concentration of solution: 100 mg Cr(VI)l^{-1}; ZER dosage: 5 g l^{-1}; temperature: 25 °C) (O : pH$_i$; ● : pH$_f$).

While the final pHs were increased with respect to the initial pHs at strong acidic conditions, a decreasing trend was observed in the values of final pHs at alkaline conditions. Such a change in the pH values may be attributed to the amphoteric character of the constituents present in the ZER. The removal yield of Cr(VI) at strong acidic conditions is very low. By increasing initial pH of solution, it was observed that the removal yield of Cr(VI) attained 100 % at the initial pH of 5.0 and 11.0. The X-ray diffraction analysis of the residual pulp obtained from the experiments carried out at initial pH 5.0 showed that this material contains krokoit (PbCrO$_4$). The residual pulp at the other pH (11.3) includes basic lead chromate (PbO·CrO$_4$). These results reinforced the presence

of different mechanisms in the removal of Cr(VI) by ZER. The removal mechanisms of Cr(VI) at acidic conditions may be described by means of chemisorption of CrO$_4^{2-}$ ions on positively charged surfaces due to the amphoteric dissociation. The concentration of Pb^{2+} ions in the treated solution is, to a large extent, dependent on the solubilisation of lead sulphate. The solubility product of lead sulphate (1.7x10^{-8}) is much higher than that of lead chromate (1.8x10^{-14}) [12]. The solubilised Pb^{2+} ions from lead sulphate in equilibrium may precipitate in the form of PbCrO$_4$ as shown in reaction (i), leading to a differential solubilisation of lead sulphate. The increase in the initial pH of solution up to 10.0 causes the surface of ZER to be negatively charged, which

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leads to a decrease in the removal yield of Cr(VI). At above pH 10.0 the removal mechanisms of Cr(VI) based on the formation of basic lead chromate is as follows

$$2Pb^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)} + 2OH^- \rightarrow PbO \cdot PbCrO_{4(S)} + H_2O \quad \text{(iii)}$$
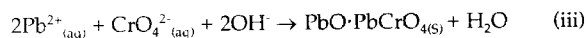
At initial pH values higher than 11.0, the removal efficiency of Cr(VI) decreased and the concentration of lead ions increased sharply, suggesting much more solubilisation of the lead sulphate and oxide, and that the basic lead chromate may not be formed due to the amphoteric character of lead. At the strong basic conditions, lead concentration reached 710 mg l^{-1}. The concentration of cadmium and zinc increased with acidity of solution due to the fact that the solubilisation rate of metal oxides are very high in the strong acidic medium. Zinc was also dissolved in significant amounts at strong alkaline conditions. If the initial pH is selected as about 11.0 for this process, the concentration of solubilised metals in the solution may be decreased under the detection limits without decreasing the yield of Cr(VI) removal. However, this pH for the system is on the edge of large scale solubilisation of lead. Therefore the pH of media must be carefully controlled. On the other hand, such alkaline treated solutions must be neutralised before discharging to the environment. In this stage, the lead ions remaining in the treated solution may be precipitated. Indeed, the concentration of lead ions (1.0 mg l^{-1}) in the solution (initial pH=11.3) was reduced under the detection limits by neutralising the solution with H_2SO_4 solution. If the removal process is carried out at acidic conditions, the treated solution must be subjected to an additional precipitation process to remove the other remained metals.

CONCLUSIONS

The data presented here show that the zinc extraction residue (ZER) containing lead compounds can be readily used for the removal of Cr(VI) from aqueous solutions. As expected, it was found that the removal percentage of Cr(VI) decreased with increase in the initial concentration of solution. However, it was observed that the Cr(VI) removal yield showed a continual increase with contact time. The ZER dosage and the temperature of solution have a positive effect on the removal yield of Cr(VI). It was found that the initial pH of solution is the most important parameter affecting the Cr(VI) removal yield. The most effective initial pHs for this process were found to be 5.0 and 11.3 with 100 % removal at 25 °C and 5 g l^{-1} ZER dosage. At initial pH 11.0, the other toxic metals are not released from ZER, but at initial pH over this value, the solubilisation of lead increased to a large extent. This situation can be considered a disadvantage. When the initial pH cannot be kept at 11.0, the toxic metals released from ZER must be eliminated from the treated solution by neutralisation.

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