

REMOVAL OF CHROMIUM (VI) WITH ALIQUAT 336 IMPREGNATED IN AMBERLITE XAD-16. I. BATCH MODE SORPTION STUDIES

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Abstract. This work investigates the removal of chromium (VI) from aqueous solutions using solvent impregnated resin (SIR). The solvent impregnated resin was formed by impregnating Amberlite XAD-16 resin with Aliquat 336 extractant. Solvent impregnated resins were prepared in three different concentrations; 0.5, 1.0 and 2.0 grams Aliquat 336 per gram XAD-16. The solvent impregnated resin was formed using the wet method. The effect of pH on the sorption of chromium (VI) ions was investigated; equilibrium experiments were carried out with the different concentrations of solvent impregnated resin to test the sorption capacity. It was found that the sorption of chromium (VI) was most effective at pH 6. It was found that 90% removal was achieved under optimal conditions. The adsorption capacity for chromium was found to be 0.47, 0.56 and 0.63 mmol/g for 0.5, 1.0 and 2.0 g/g, respectively.

Keywords: Chromium (VI), solvent impregnated resins, Aliquat 336

Abstrak. Kertas kerja ini adalah untuk mengkaji penyingkiran kromium (VI) dengan menggunakan *solvent impregnated resin* (SIR). SIR dihasilkan dari penyilangan antara resin *Amberlite XAD-16* dengan *Aliquat 336 extractant*. SIR disediakan dalam tiga kepekatan yang berbeza iaitu 0.5, 1.0 dan 2.0 gram *Aliquat 336* gram XAD-16. Penyilangan SIR disediakan secara kaedah basah. Kesan terhadap pH untuk penyerapan kromium (VI) dikaji serta eksperimen keseimbangan untuk tiga kepekatan berbeza telah dijalankan. Kajian mendapati penyerapan kromium (VI) paling berkesan pada pH 6 di mana sebanyak 90% penyingkiran berlaku pada tahap optimal. Kapasiti penyerapan kromium (VI) adalah 0.47, 0.56 dan 0.63 mmol/g untuk 0.5 g/g, 1.0 g/g and 2.0 g/g.

Kata kunci: Kromium (VI), *solvent impregnated resins*, *Aliquat 336*

1.0 INTRODUCTION

The tannery industry generates large amounts of wastes that can harm nature and human health. Chromium, a metallic element primarily found in nature in two oxidation states (III and VI), is a major constituent. The toxicity of this element is a function of its oxidation states, chromium (VI) species being the more toxic. Tannery waste contains

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only trivalent chromium. However, the regulations on the disposal of such wastes are based on the probable presence of hexavalent chromium. In order to avoid the uncontrolled waste of this type of pollutant, it is necessary to develop techniques that allow its recovery and reutilization in the productive chain.

Solvent extraction and ion exchange techniques have been mostly applied to the recovery and separation of metal ions. However, recovery and separation by solvent extraction requires multi extraction and back extraction in order to get successful separation [1]. Other major drawback of solvent extraction is the loss of extractant/solvent in large-scale industrial applications. The small but finite aqueous solubility of extractants, diluents and modifiers is a major disadvantage of solvent extraction [2]. Moreover, solvent extraction is inefficient at trace metal ion concentrations because of excess solvent requirement [1]. To reduce this loss, several novel techniques have been studied; e.g. a nondispersive solvent extraction system that involves contacting the effluent with a hollow fibre modules have been prepared and tested for the solvent extraction of Cr (VI) using Aliquat 336 as the extractant [3].

As an alternative approach, extractant impregnated resins have been proposed by Warshawsky for selective separation of metal ions by direct adsorption of the extractant into macroporous polymeric support [4]. They combine not only the advantages of resin ion exchange for processing dilute solutions with specific properties of the extractant, but also high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristics of solid ion exchange technology. It has been recognized that the impregnated extractants can exhibit strong affinity for the polymeric matrix but still behave as if in the liquid state [4]. The concept of impregnated resins was developed out of need for ion-specific resins, the availability of suitable polymeric carriers and from the deficiency in suitable methods for chemical functionalization of polymeric carriers. Physical impregnation on selected polymeric carrier, which provides "solvent impregnated resin". The name was chosen to emphasize the extractant (solvent), method (impregnation), and function (ion exchange resin) [4].

Among the supports that fulfill those characteristics are macroporous polymers of the styrene-divinylbenzene (Diaion HP-20), hydrophobic methacrylic based (HP-2MG) and XAD matrices [2, 5, 6, 7]. Very recently, it was reported that solvent impregnated resins containing Aliquat 336 were prepared using Amberlite XAD-7 as a polymeric support to Cr (VI) extraction from aqueous solution [1].

Amines of high molecular weight have been extensively investigated for the removal of Cr (VI) and several economic studies have shown the viability of the Cr (VI) recovery from washing operations of final metallic products. Kabay and co-worker also have prepared SIR that employed Aliquat 336 as the extractant and acetone as the solvent for impregnation [2]. Batch sorption studies have shown that solvent impregnated resins containing Aliquat 336 can be effectively used for the removal of hexavalent chromium from aqueous solutions [1].

In this work, Amberlite XAD-16 was used to prepare the SIR for removal of Cr (VI) ions from aqueous solution using Aliquat 336 as an extractant and acetone as the solvent. In this work, the effect of pH on the sorption of chromium (VI) ions has been investigated and equilibrium experiments have been carried out with different concentrations of solvent impregnated resin to test the sorption capacity.

2.0 EXPERIMENTAL

2.1 Materials

Amberlite XAD-16 and Aliquat 336 were supplied by Sigma Aldrich Co. Potassium Chromate (K_2CrO_4) used to prepare chromate solution was supplied by Sigma Aldrich Co. Hydrochloric acid and sodium hydroxide were used to control pH of Cr (VI) solutions.

2.2 Impregnation Process

In this study, Amberlite XAD-16 resins were washed with absolute ethanol for 6 hours. It was then filtered and air-dried overnight. Amberlite XAD-16 resins were dried out further in vacuum oven at 313 K and an absolute pressure of 25 mm Hg for 24 hours.

Two concentrations of SIR were prepared for each size range; 0.5 g/g (Aliquat 336 to XAD-16), 1 g/g SIR and 2.0 g/g SIR. 10 g of dry Amberlite XAD-16 resins were immersed into 50 ml of acetone containing different amounts of Aliquat 336. The mixture was shake at 303 K for 24 hours. The SIR beads were separated by filtration using sintered glass funnel and washed with deionized water. The resins obtained were first air-dried and then dried under vacuum at 313 K.

2.3 Analysis

Atomic absorption spectrophotometer (Varian SpectraAA-200) was used for Cr (VI) concentration in solution. The pH of the solution was measured using a Mettler Toledo 340 pH meter.

2.4 Effect of pH on the Sorption of Cr (Vi)

Solutions of 10^{-4} molar potassium chromate were prepared at pH 2, 4, 6 and 8 to study the effect of pH on the adsorption of Cr (VI). 40 mg of each concentration SIR (0.5 g/g and 1 g/g) were contacted with 25 ml of each pH solution for a period of 24 hours. For this time, the solutions were agitated in a constant temperature shaker, set at 100 rpm and 26°C. The amount of chromium remaining in the solution was measured using an Atomic Adsorption Spectrometer (AAS). The initial concentration of chromium in each solution was also measured.

2.5 Equilibrium Study

Solutions of chromium (VI) were prepared with various concentrations (10^{-4} – 0.004 M). From the results of the pH study, it was decided to investigate the equilibrium studies at pH 6. pH 6 was chosen as the amount of chromium (VI) removed at this pH was high. 25 ml of each solution were placed in a 50 ml conical flask. 0.04 g of 0.5 g/g SIR was added to each solution. The solutions were placed in a constant temperature shaker and shake at 26°C and 100 rpm for 24 h. The experiments were duplicated with 0.04 g of 1.0 g/g SIR making two sets of solutions in total. After 24 hours, the SIR was removed from the solution. The pH of the solution was recorded and the amount of chromium remaining in the solution was measured. The initial and final concentration of chromium in each solution was measured.

3.0 RESULTS AND DISCUSSION

3.1 Preparation of Solvent Impregnated Resin

Nitrogen analysis was performed to determine the amount of Aliquat 336 adsorbed by the XAD-16 resin. The theoretical amount of nitrogen was determined based on the increase in the mass of the resin after the impregnation. This is then compared to the results of the Kjeldahl method, which determines the actual amount of nitrogen present within the resin. If the results are similar then the impregnation process can be said to be successful as the mass of nitrogen in the XAD-16 is due to the Aliquat 336. Table 1 shows the results of each test, there is a maximum error from the theoretical value of 7.83%. The percentage error was computed based on the difference between the theoretical value and those obtained from Kjeldahl method.

The most reliable and convenient tool for the study of the physical structure of SIR beads is the scanning electron microscope (SEM). Micrographs of the bead surface are taken directly, and micrographs of the beads internal structure are taken on fractured beads. SEMs were taken on a Cambridge Instrument stereo scan 360 microscope at room temperature. Figure 1 shows SEM of 0.5 g of Aliquat 336 impregnate on XAD-16. The micrograph shows a perfect round shape of SIR beads without surface defect. The structure of the impregnated polymeric support can change radically only if the support allows considerable expansion or contraction during the impregnation process.

Table 1 Results for nitrogen analysis

Cylinder	SIR (g Aliquat 336/g resin)	Mass (g)	Kjeldahl nitrogen (% mass)	Theoretical nitrogen (% mass)	Error from theory (%)
1	0.5	0.150	0.420	0.43	2.26
2	1.0	0.150	0.701	0.76	7.83
3	2.0	0.150	0.981	1.04	5.70

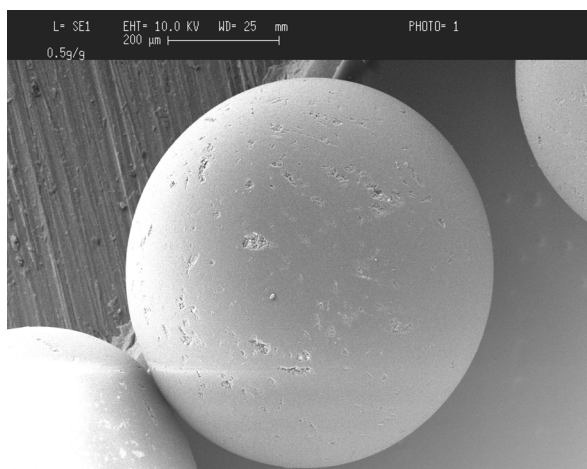
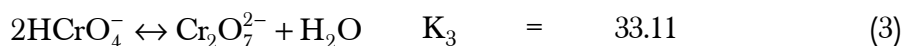
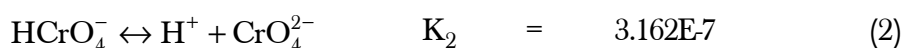
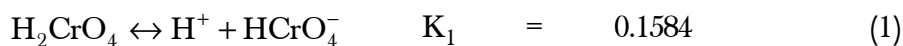


Figure 1 External shape of 0.5 g/g SIR with magnification X110

Thus, only gel or gel-analogue supports are expected to undergo structural modification during the impregnation, whereas the stable macroporous supports or fictionalized macroporous supports are expected to show little structural changes.

3.2 Effect of pH on Cr (VI) Removal by Solvent Impregnated Resin

Hexavalent chromium, Cr (VI), may exist in the aqueous phase in different forms; the total amount of chromium and the pH are the main variables of the chromium species in an aqueous phase. The following are the important equilibrium reactions [3].



Since the distribution of chromate species is dependent on both the pH and total Cr (VI) concentration, a predominance diagram (Figure 2) is presented using both pH and total Cr (VI) as variables [3]. It is necessary to understand the solution chemistry of hexavalent chromium in order to explain the binding mechanism of chromate by various adsorbents or ion exchange materials.

It may be noted that HCrO_4^- and CrO_4^{2-} are by far the most predominant species at this total Cr (VI) concentration, the relative predominance of each varying with pH.

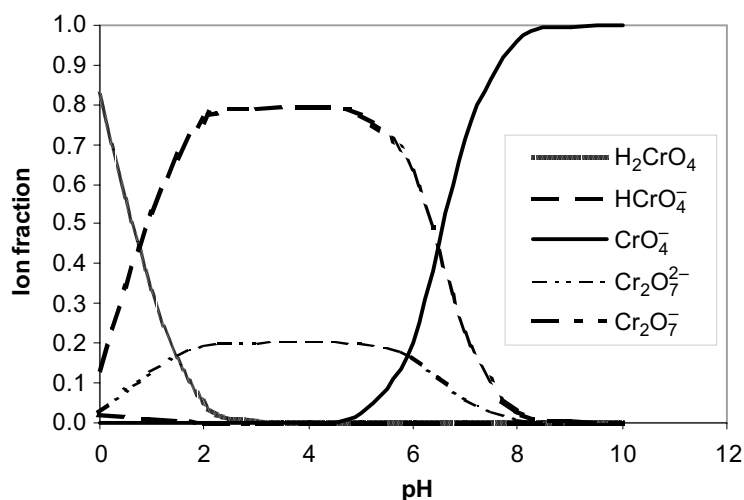
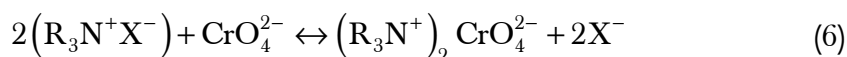


Figure 2 Speciation diagram for a 0.001M Chromium (VI) solution

None of the polymeric forms of chromate, namely, CrO_7^{2-} , $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ are present to any significant degree in the aqueous phase at concentration of 0.001 mol/L.

Vincent and Guibal [8] reported that solution pH is a key parameter for the efficient extraction of Cr (VI) using Aliquat 336 as the carrier in a hollow fibre module and, moreover, stated that pH should be maintained below 4.5. Vincent and Guibal noted that the decrease in extraction efficiency above pH 5 is related to the speciation of Cr (VI) and especially to a decrease in the fractions of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ with increasing pH. However, Kabay and co-workers reported that they did not obtain any decrease in Cr(VI) removal above pH 5, they had concluded that SIR can easily remove Cr(VI) above neutral pH conditions when chromate is mainly present as CrO_4^{2-} ion [2].

From Figure 3, it is clearly shown that there was a distinct decrease in Cr (VI) removal at an equilibrium pH below 4. Vincent and Guibal also observed this decrease in acidic solution and explained it by considering that protonated amine groups are saturated by counter anions present in the solution and also the reduction of Cr (VI) to Cr (III) is strongly increased. In addition, the decrease in Cr (VI) extraction at acidic pH may be explained by the fact that Cr (VI) will form H_2CrO_4 as a non-anionic species and therefore, does not take part in the anions-exchange process. The anions exchange reactions involved in the process depend on chromate speciation in solution as given in Equations (5) and (6) [2]:



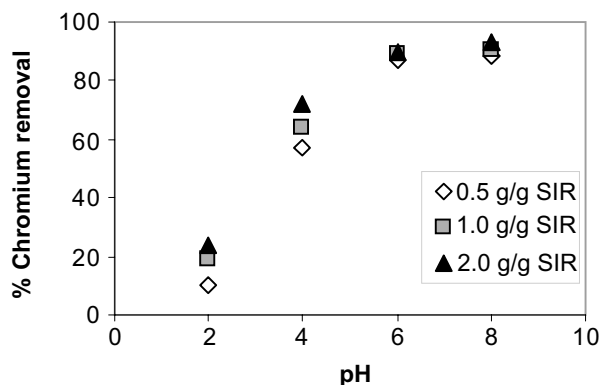


Figure 3 Effect of pH on chromate removal by SIR

3.3 Equilibrium Study

Equilibrium data was obtained for Cr (VI) adsorption onto solvent impregnated resins at pH 6. The Langmuir model is given by Equation (7) and was used to correlate the equilibrium data obtained.

$$\frac{q}{q_{\max}} = \frac{bC_e}{1 + bC_e} \tag{7}$$

Where, C_e is the equilibrium concentration (mmol/L), q is the amount of chromium removed at equilibrium per mass unit SIR (mmol/g) and q_{\max} , b are the Langmuir constants related to sorption capacity and energy of sorption, respectively.

Figure 4 shows that the Langmuir model fits the data well yielding regression values, which are shown in Table 2. The experimental results indicate that the maximum

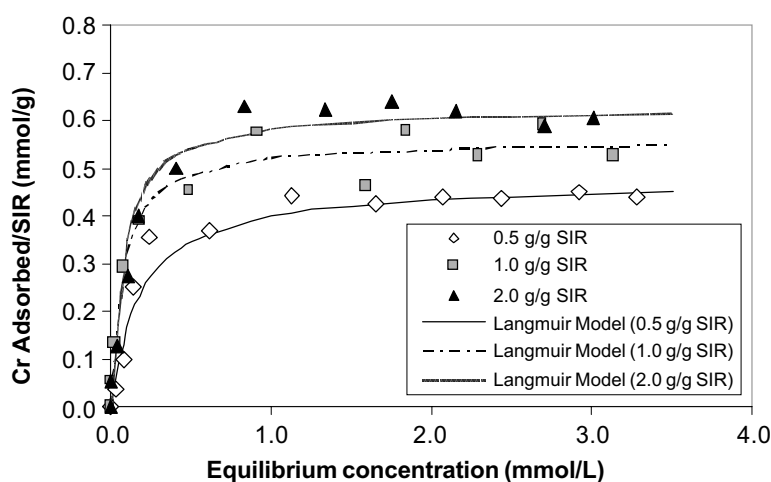
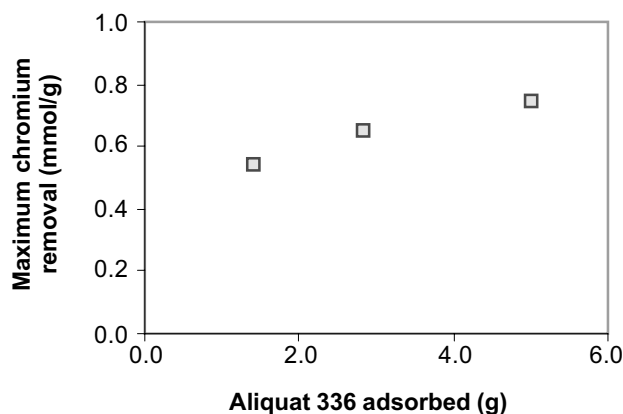


Figure 4 Adsorption isotherm for 0.5 g/g, 1.0 g/g and 2.0 g/g SIR

Table 2 Langmuir equations constants for equilibrium experiments

SIR (g/g)	Aliquat 336 adsorbed (g)	q_{max} (mmol/g)	b (l/mmol)	Langmuir regression (R^2)
0.5	1.4173	0.4728	5.4790	0.9956
1.0	2.8276	0.5586	13.1335	0.9877
2.0	4.3122	0.6296	12.5648	0.9963

uptake values were 0.47, 0.56, 0.63 mmol Cr (VI) per g SIR for SIR prepared at 0.5, 1.0 and 2.0 (g Aliquat 336/g polymer), respectively. It clearly shows that sorption capacity of SIR increased with increasing ratio of impregnation. Figure 5 shows that the maximum chromium removal increased with the increase of Aliquat 336 adsorbed.

**Figure 5** Plot of grams of Aliquat 336 adsorbed against maximum chromium uptake

4.0 CONCLUSION

SIR containing Aliquat 336 was found to be a promising sorbent for the removal of Cr (VI) from aqueous solutions. The impregnation of XAD-16 with Aliquat 336 extractant was successful for all solution strengths as the Aliquat uptake increased linearly with impregnation solution strength.

The 2.0 g/g SIR suffered from leaching of extractant, which shows that stabilization needs to be applied if concentrations of 2.0 g/g SIR and above are to be used effectively. At pH values below 4, the efficiency of chromate ion removal dropped drastically. The Langmuir Model proved a good correlation for the experimental equilibrium data. A positive linear relation was obtained between the amount of Aliquat 336 present in the XAD-16 resin and the amount of chromium removed by the SIR.

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