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Removal of Chromium (Vi) From Aqueous Solution By Sorption on To Selective Silver Resin

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Abstract:*This study investigate the removal efficiency of chromium (VI) from water by using (R-AgCl) Silver chloride resin (SCR) as selective sorbent material for removal chromium (VI) from aqueous solution; the study was carried out by sorption batch experiments at room temperature(25°C). Efficiency of Cr(VI) removal was determined by measuring the chromium concentration before and after the sorption process. Atomic absorption spectroscopy (AAS) method has been applied as analytical method for determination of Cr concentration in water. Governing factors for removal efficiency were proposed, analyzed and compared. It was conducted that the process is mostly affected by pH value of solution, mass of sorbent and concentration of Cr(VI) , which was the most efficient sorbent showed maximal efficiency and maximal sorption capacity, 1.5g of SCR after 60 min at 25 °C and pH 6.5 recovered 98% of Cr(VI) from 100 mL of water polluted with 20 mg of Cr(VI).*

Keywords: *Chromium (VI), Removal, Water, Silver chloride , AAS, Batch system*

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I. Introduction

Chromium exists in two major stable oxidation state, Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because this form is hazardous to health. Strong exposure of Cr(VI) causes cancer in digestive tract , lungs and also may cause ephgastricpain nausea, vomiting, severe diarrhea, hemorrhage [1] and bladder tissue [2]. The Cr(VI) forms are more toxic than the Cr(III) forms [3]

Chromium exist in to the natural bodies of water from industries such as electroplating[4], leather tanning[5], pigments paints, fungicides, cement industries, steel industries, and photography [6]. It found naturally in plants, rocks, soil and volcanic dust.

Water soluble chromium species existing in natural water are Cr(VI) as CrO_4^{2-} or $HCrO_4^-$ and Cr(III) as $Cr(OH)_n^{(3-n)+}$. The distribution of chromium depends on the redox potential and pH value [7]. The Chromium speciation diagram shows that , in the pH range of 3-8, the Cr (VI) is present mainly in anionic forms of ($HCrO_4^-$) and (CrO_4^{2-}) [8].

Find easy and simple methods for removing chromium from environment has become great concern. Various technology are employed for removing Chromium such as ion exchanges [9-12], activated carbon [13], filtration, biological [14], pyrite, and other adsorption methods [15-17]. Various sorbent materials, including iron and aluminum hydroxide, have a strong affinity for dissolved chromium. Chromium is strongly attracted to sorption sites on the surface of these solids [18], hydrated iron(III) oxide of HFO is expensive, available and chemical stable over a wide pH range. Many previous studies confirmed that Iron(III) oxides have high sorption affinity toward chromium [18] Electrochemical removal is one of the most procedure for removing of Cr by using carbon aero gel electrodes [19]

All the removal technology have added benefit for removing other undesirable compound along with Cr depending on the technology such as bacteria, turbidity, color, odor , hardness, phosphate, fluoride, nitrate and other ions can be removed [5],

This study reports the use of R-AgCl resin (SCR) as a selective sorbent material to remove Cr(VI) from aqueous solutions. Simplified scheme of the SCR process based on the activity of resin, the selectivity resin is based on chemisorption on the particles, by selective binding of ionic forms of Cr(VI).

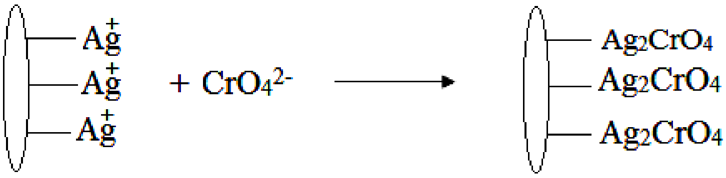

Fig.1. Scheme of the sorption of Cr(VI) on the surface of SCR

II. Experimental

Chemicals

The chemical compound used in this experimental work were: $AgNO_3$, (Riedel-de Haen); K_2CrO_4 (p.a., Aldrich; HCl 1:1 (Merck); HNO_3 1:1 (Merck); NaOH (Merck).

Chromium (VI)

Cr(VI) stock solution (1000 mgL^{-1}) was prepared by dissolving 3.73g of potassium chromate K_2CrO_4 (p.a., Aldrich); in 1L volumetric flask with distiled water and refrigerated in an amber bottle.

Sorption resin (SCR) Batch system

The SCR used in experimental work was prepared according to [20]. Chromium sorption process was investigated in the batch system. Sorption in the patch tank was conducted with range 1.0-20 mgL^{-1} Cr(VI) concentration of 100 mL solution was placed in Erlenmeyer flask (500 mL). The resins were measures and added to Cr(VI) solution, the pH analysis were conducted within range 2.0 to 9.0, the pH adjustments were accomplished with 0.1 M HCl or 0.1 M NaOH, mass of sorbent was tested (varied from 0.5 g to 2.0 g). The effects of temperature influence on sorption efficiency were tested at (25, 30 and 35 °C), sample was then shacked in laboratory shaker(150 rpm) for 60 min.

Exchange and sorption capacity was determined according to the following equation:

$$q = \frac{C_i - C_f}{m}$$

Where: q: sorption capacity, g/g. C_i : initial Cr(VI) concentration, mg.
C_f : final Cr(VI) concentration, mg. m: mass of SCR, g

III. Results and Discursion

pH effect

The effect of pH value of distilled water polluted with Cr(IV) on SCR process was studied and presented in Fig.1 (m=1.0 g) of SCR, volume of solution was (V=100 mL), temperature (room temperture 25°C), contact time (60 min), shaker speed (150 rpm) and the concentration of Cr(VI) (20 mgL^{-1}).

The pH value was varied between pH 4.0 to 9.0. The efficiency of SCR at different pH value for removing Cr(VI) from water is calculated, and the percent % of Cr(VI) removed from water sample is presented in Fig.2

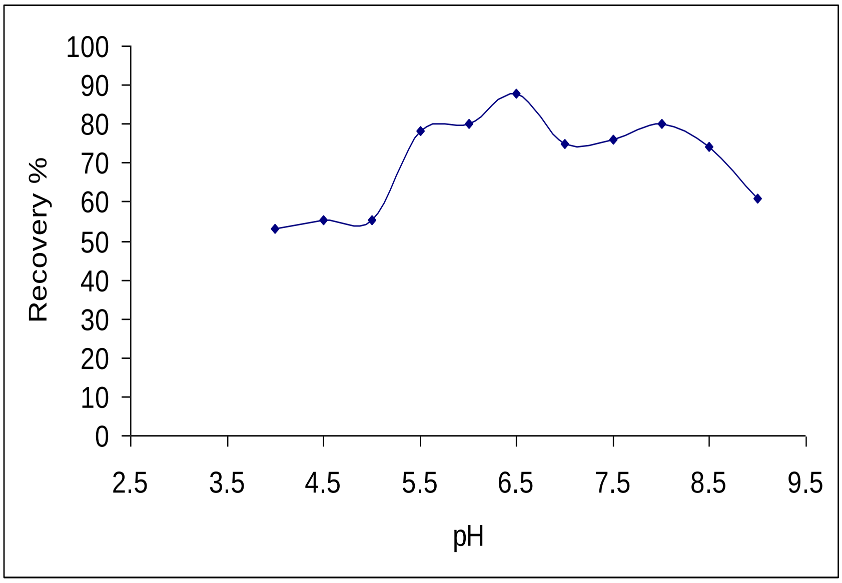

Fig.2 Effect of pH for Removing of chromium (VI) by using SCR.

It found that, the removal of Cr(VI) by using SCR is not affected by pH 3.0 to 5.0 comparing to pH value of 6.0 to 7.0, the Cr(VI) species are more senstive to the neutral of pH than Cr(III) which were expected, the efficency removal of Cr(VI) at pH 6.5 is reached to 90% and at pH 7.0-8.0 up to 75%, while the effeciency removal at pH 4.0-5.0 was less than 55%.
It is in good agreement with the fact that the chromium species are in Cr(VI) form in this range of pH.

Mass of resin (SCR) effect

The effect of mass of SCR on removal process was studied (pH of water was constant 6.5 , concentration of Cr(VI) (20 mgL^{-1}), volume of solution (V=100 mL), contact time (60 min), temperature (room temperature), shaker time (150 rpm) and mass of SCR was varied (0.5g, 1.0g, 1.5g, and 2.0g). For each mass, the efficiency of SCR to remove Cr(VI) from water is calculated, and is presented in Fig.3.

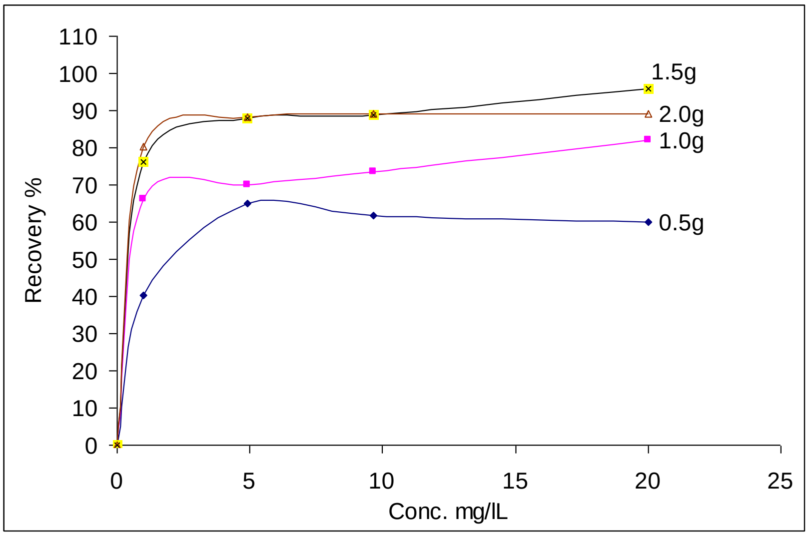

Fig.3 The capacity of SCR for removing Cr(VI) at various mass.

Fig.3 shows that the influence of mass of SCR in removal of Cr(VI) is high affected by mass if resin. Where the removal capacity was up 95.9% for 1.5 g if SCR comparing with 60%, 82% and 89 % for 0.5g, 1.0g and 2.0g respectively.

Effect of temperature

The effect of temperature on the removal process performance was examined and presented in Fig.4. the experimental conditions were the mass of SCR (m=1.5 g), pH of water (pH 6.5), concentration of chromium (20 mgL^{-1}), volume of water (V=100 mL,), contact time (60 min), shaker speed was (150 rpm), Temperature was varied between 25°C ,30°C and 35 °C.

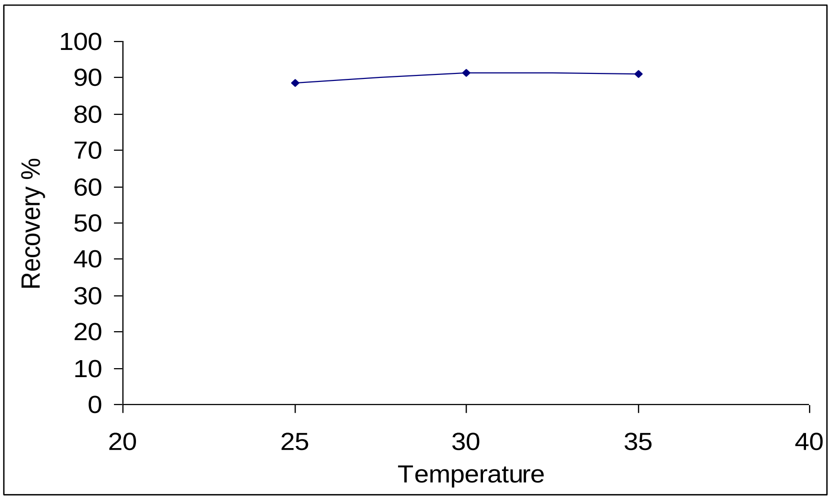

Fig.4. The effect of temperature on removal process.

The result shows that the removal of Cr(VI) is stable as the temperature between 25-35°C. and it was found that the color of SCR bed become dark brown when temperature was reached up to 30°C

Optimum procedure

An easy and simple method for removing Cr(VI) from water has been applied to standard solutions and real water samples. at room temperature, mass of SCR (1.5 g), volume of water sample (100 ml), pH 6.5 fillled in batch system with contact time (60 min), and shaker speed was (150 rpm).

Application of proposed method to standard solution samples

Five samples of standard solution spiked with different concentration of Cr(VI) were prepared to check the efficiency of Cr(VI) removal. The procedure was based through to approach concentration of Cr(VI) in water, the spiked range was 1.0 –20 mgL^{-1}, the results of standard five sample are shown in table 1.

The results show that, the good recoveries of 96.8, 99.6, 94.6, 97.3, 107.4 % were obtained and RSD were 3.7, 3.0, 5.0, 0.7, 1.9 % of standard solution 1.0 , 5.0, 10 , 15 , 20 mgL^{-1} respectively.

Table 1. Results of the proposed removal procedure by SCR resin in spiked standard solution.

Standard Solution	Spiked Standard Solution.		
	Cr(VI) Added Mgl^{-1}	Removed Mgl^{-1}	Recovery (%)
1	1.0	0.97±0.04	96.8
2	5.0	4.98±0.14	99.6
3	10	9.46 ±0.48	94.6
4	15	14.6±0.11	97.3
5	20	21.48 ±0.41	107.4

Interference

Effect of Chloride

As we known the SCR (Ag^+) is preferred react with chloride (Ksp $1.8X10^{-10}$M) over Cr(IV). The effects of the varying concentration of chloride ion on the removal of Cr(VI was studied and presented in Fig. 5.

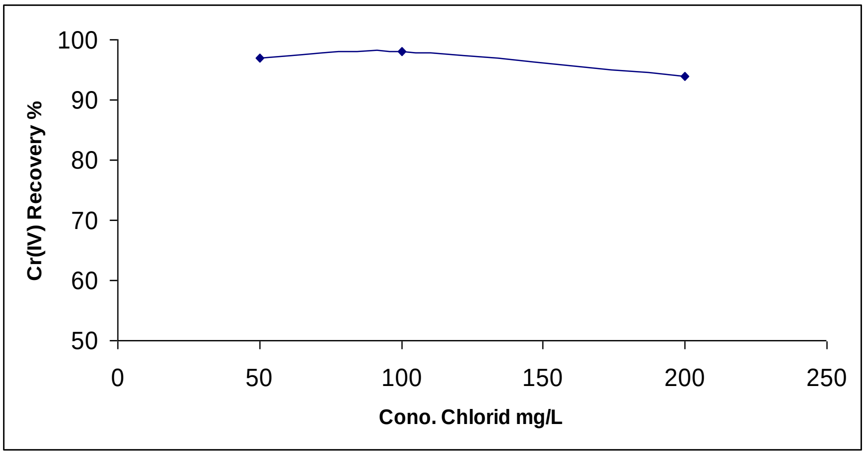

Fig.5. The effect of Chloride on removal process.

The influence of Chloride ion on the Chromium (IV) ion sorption efficiency was investigated by using solution containing, mass of SCR (1.5 g), concentration of Cr(IV) (20 mgL^{-1})Volume of water (100 mL), temperature (room temperature) and contact time(60 min) , (pH 6.5) , shaker speed (150 rpm) and the concentration of chloride was (50 mgL^{-1}, 100 mgL^{-1}, 200 mgL^{-1}). The efficiency of SCR to adsorbed Cr(IV) from water is calculated, and the 200 mgL^{-1} of chloride not have any major effect on Cr(IV).

Application to real water samples After evaluating the main features of the proposed removal procedure , the application to the drinking water samples were applied.

Table 2. Presented results of Cr(VI) species removal in five real drinking water samples spiked with different concentration of chromium.

Table2. Analytical data of removal Cr(VI) using SCR in real water spiked with different concentration of chromium.

Water sample	Cr content standard addition mgL^{-1}	Removed mgL^{-1}	Recovery (%)
1	1.0	1.09 ±0.06	109
2	5.0	4.61 ±0.27	92
3	10	10.2±0.19	102
4	10	10.06 ±0.151	100.6
5	20	19.66±0.24	98.3

The recovery of real water samples were good , with RSD values of 5.7, 5.9, 1.8, 1.5, and 1.22 % respectively

IV. Conclusion

The aim of this paper was the removal of Cr(VI) species from water by using selective sorption resin (SCR), the removal was accomplished by adjusting the pH of water sample. In order to large the choice of sorbent for Cr(VI) adsorption a specific task of this study was to analyze, extract the best feature of SCR. Results obtained suggest that, the SCR is the most efficient for Cr(VI) removal; excellent feature is the fact that this SCR cover neutral pH of water and it is efficient. The removal process showed that the SCR could be used for removing of the concentration of Cr(VI) in Chromium standard solution prepared in laboratory and in drinking water samples spiked with different concentration of Cr(VI). It has sorption capacity 1.5 g of SCR after 60 min at room temperature and pH 6.5 sorbed 98% of Cr(VI) from 100 mL of water polluted with 20 mgL^{-1} of Cr(VI). Chemical adsorption on to SCR (chemisorption on R-AgCl) is favorable process (sorption efficiency stable with temperature range 25°C, 30°C° and 35°C).

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