

Adsorption of chromium trivalent cation on surface of zirconium oxide

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Abstract: The potential of zirconium oxide as a low-cost adsorbent for the removal of a Cr^{3+} ion from aqueous solution was investigated in this study. The influences of pH, initial metal concentration, and temperature were studied in batch experiments. About 98.95 to 99.97 adsorption achieved by using 0.2 g adsorbent. This study shown that adsorption increases as the initial metal ion concentration increased. This study was also carried out at different pH ranges (3.0 – 10.0) and about (98.91–99.71%) adsorption was occur at different pH scale. The effect of temperature from (20 – 50°C) was also performed in this research. And we come to know that about 98% adsorption was obtained at 20°C, the adsorption efficiency was gradually decreased with increasing temperature, and percent removal was reached up to 97.71% at 50 °C.

Keywords: Zirconium, Chromium, Cation, Adsorption.

I. INTRODUCTION

Zirconium is sometimes known as zirconia, is a white crystalline oxide of zirconium. Its most naturally occurring form, with a monoclinic crystalline structure, is the mineral baddeleyite. A dopant stabilized cubic structured zirconia, cubic zirconia, is synthesized in various colors for use as a gemstone and a diamond simulant. Zirconia is produced by calcining zirconium compounds, exploiting its high thermal stability [1]. Three phases are known: monoclinic < 1170 °C, tetragonal 1170°C–2370 °C, and cubic >2370 °C. The trend is for higher symmetry at higher temperatures, as is usually the case. A few percentages of the oxides of calcium or yttrium stabilize the cubic phase. The very rare mineral tazheranite (Zr, Ti, Ca) O₂ is cubic. Unlike TiO₂, which features six-coordinate Ti in all phases, monoclinic zirconia consists of seven coordinate zirconium centers. This difference is attributed to the larger size of Zr atom relative to the Ti atom [2]. Zirconia is chemically unreactive. It is slowly attacked by concentrated hydrofluoric acid and sulfuric acid. When heated with carbon, it converts to zirconium carbide. When heated with carbon in the presence of chlorine, it converts to zirconium tetrachloride. This conversion is the basis for the purification of zirconium metal and is analogous to the Kroll process [3]. Chromium is a chemical element which has the symbol Cr and atomic number 24. It is the first element in Group 6. It is a steely-gray, lustrous, hard and brittle metal which takes a high polish, resists tarnishing, and has a high melting point. The name of the element is derived

from the Greek word chroma, meaning colour because many of its compounds are intensely coloured.

Chromium oxide was used by the Chinese in the Qin dynasty over 2,000 years ago to coat metal weapons found with the Terracotta Army. Chromium was discovered as an element after it came to the attention of the western world in the red crystalline mineral crocoite (lead (II) chromate), discovered in 1761 and initially used as a pigment. Louis Nicolas Vauquelin first isolated chromium metal from this mineral in 1797. Since Vauquelin's first production of metallic chromium, small amounts of native (free) chromium metal have been discovered in rare minerals, but these are not used commercially. Instead nearly all chromium is commercially extracted from the single commercially viable ore chromite, which is iron chromium oxide (FeCr₂O₄). Chromite is also now the chief source of chromium for chromium pigments [4].

Chromium metal and ferrochromium alloy are commercially produced from chromite by silicothermic or aluminothermic reactions or by roasting and leaching processes. Chromium metal has proven of high value due to its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding metallic chromium to form stainless steel. This application, along with chrome plating (electroplating with chromium) currently comprise 85% of the commercial use for the element, with applications for chromium compounds forming the remainder. Trivalent chromium Cr(III) ion is possibly required in trace amounts for sugar and lipid metabolism, although the

issue remains in debate. In larger amounts and in different forms, chromium can be toxic and carcinogenic. The most prominent example of toxic chromium is hexavalent chromium (Cr (VI)). Abandoned chromium production sites often require environmental cleanup [5]. Adsorption techniques for wastewater treatment have become popular in recent years due to their efficiency in the removal of pollutants that are too stable to be removed by biological methods. Adsorption is a process that occurs when a gas or liquid solute adheres to a surface (adsorbent), forming a molecular or

atomic film (adsorbate). This process differs from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption occurs naturally but industrialists have perfected adsorption methods to clean up hazardous waste in wastewater or purify drinking water. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility, simplicity of design, ease of operation and insensitivity to toxic pollutants [6].

II. METEIRAL AND METHOD

Current studies were carried out department of chemistry kohat university of science and technology kohat, Khyber Pakhtunkhwa, Pakistan

Sample collection

The zirconium oxide and chromium chloride were issued from chemistry department.

Buffer solution of pH 7

By preparing 0.1 molar solution of NaOH and 0.1 molar solution of potassium dihydrogen phosphate. Then 29 mL from NaOH solution and 50 mL from KH₂PO₄ solution were mixed it gives pH 07 buffer solution.

Buffer solution of pH 10

By mixing 50 mL of 0.05 M solution NaHCO₃ with 10.7 mL of 0.1 M solution of NaOH give buffer of pH 10.

Preparation of 1000 ppm chromium solution

1000 ppm solution of potassium was prepared by dissolving 5.126 g of solid chromium chloride in 1000 ml of volumetric flask and diluted it up to the mark with distilled water. This was we called the stock solution and further more ppm solutions were prepared from this solution by the following formula:

$$C_1V_1 = C_2V_2$$

Where C₁ = 1000 ppm stock solution

V₁ = ml taken from stock solution

C₂ = required ppm solution

V₂ = required volume of distilled water in ml

$$C_1V_1 = C_2V_2$$

$$1000 \times V_1 = 100 \times 100$$

$$V_1 = 10000/1000$$

$$V_1 = 10 \text{ ml}$$

So by taking 10 ml from stock solution and dissolve in distilled water and raise the volume to 100 ml will make 100ppm solution. Furthermore ppm solution was prepared from this formula such as below.

Table 1: Different ppm solution from 1000 ppm potassium solution

S. No	ppm Solution	(ml) of stock solution taken	Dissolved in distilled water (ml)
1	10	1	100
2	20	2	100
3	40	4	100
4	60	6	100
5	80	8	100
6	100	10	100
7	150	15	100
8	200	20	100
9	250	25	100

Preparation of zirconium oxide solution

Zirconium oxide solution was prepared by dissolving 0.2 g of zirconium oxide in 50 ml of required ppm solution.

Concentration

In first step the pH meter was calibrated with pH 7.0 and 10.0 buffer solution.

In the 2nd step all the apparatus were washed by distilled water. Then 50 ml solutions of potassium which were of 10,20,40,60,80,100,150,200,& 250 ppm were taken in a beaker and added 0.2g of sample.

In 3rd step beakers containing solution were kept on a shaker for the purpose of adsorption. The pH of these

solutions i.e. 10, 20,40,60,80,100,150,200 & 250 ppm was measured after each interval of time.

Temperature

In first step the pH meter was calibrated with pH 7.0 and 10.0 buffer solution.

In the 2nd step all the apparatus were washed by distilled water. Then 50ml solution of potassium (100ppm) was taken in a beaker and added 0.2g zirconium oxide sample. These solutions were kept on a hot plate stirrer for the purpose of adsorption and for maintaining the temperature up to 10,20,30,40 & 50 centigrade.

In 3rd step the pH of these solutions were measured after each interval of time.

pH

In first step the pH meter was calibrated with pH 7.0 and 10.0 buffer solution.

In the 2nd step all the apparatus were washed by distilled water. Then 50 ml solution of potassium (100 ppm) was

taken in beaker and added 0.2g of sample. The pH of solutions were stabilized to 3,4,5,6,7,8,9 & 10 in a separated beakers by acidic and basic (0.1N) solution.

III. RESULT AND DISCUSSION

Effect of initial metal ions concentration on percent adsorption

The percent removal of Cr⁺³ was studied as a function of initial metal ions concentration. The experiments were carried out using metal ion solutions ranging from 10 to 250 mg/L at room temperature 25° C (298 K). The metal ions removal capacity of zirconium is presented as a function of initial ions concentration of Cr⁺³ in aqueous solution in Figure 1 and Table 2. It is observed that the percent sorption of the metal ions increase as we increase

the initial concentration of the metal. This may be due to the fact that small amount of zirconium powder has enough capacity to adsorb high concentration of Chromium. It is observed in Figure 1 that there is gradual increase in adsorption of Chromium as the concentration of Chromium increase from 10 to 250ppm which shows that zirconium has a special affinity towards chromium ions.

Table 2: Effect of initial metal ion concentration in the adsorption of Cr⁺ at 298

Concentration(ppm)	% ads of k at 298 K ⁺
10	98.95
20	99.20
40	99.30
60	99.40
80	99.50
100	99.60
150	99.87
200	99.91
250	99.97

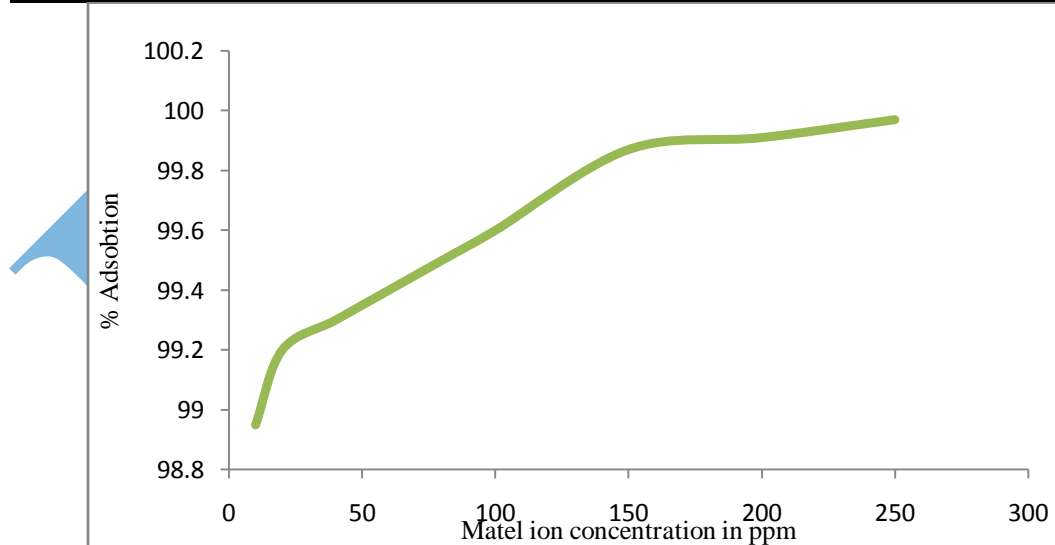


Figure 1: Effect of initial metal ion concentration in the adsorption of Cr⁺³ at 298 K

Effect of Solution pH on percent adsorption

Solution pH is an important process parameter in adsorption, since it is responsible for protonation of metal binding sites, metal speciation and degree of ionization in solution. The effects of pH on the amount of Cr⁺³ ions adsorbed were analyzed over the pH range

3–10. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. The results were presented in Figure 2 and Table 3.

Figure 2 shows that the effect of pH on the adsorption of chromium ions onto zirconium oxide from aqueous

solutions. Removal of chromium ions (initial ion conc. 100ppm) is above 99% at pH above 3.0 and at lower pH the percent removal was 98%. This means that at below pH 3.0 the percent sorption is decreases and sorption increases greatly with increasing pH. Such increase in adsorption can be attributed to the favorable change in surface charge and to the extent of hydrolysis of the adsorbing metal ion. As shown in the figure, the surface charge becomes more negative with an increase in pH. This would enhance surface attraction of monovalent metal cations for adsorption.

Table 3: pH effect of Cr⁺³ ions on zirconium oxide (initial concentration=100ppm).

pH	% adsorption of K ⁺
3.0	98.81
4.0	98.95
5.0	99.20
6.0	99.42
7.0	99.50
8.0	99.71
9.0	99.75
10.0	99.78

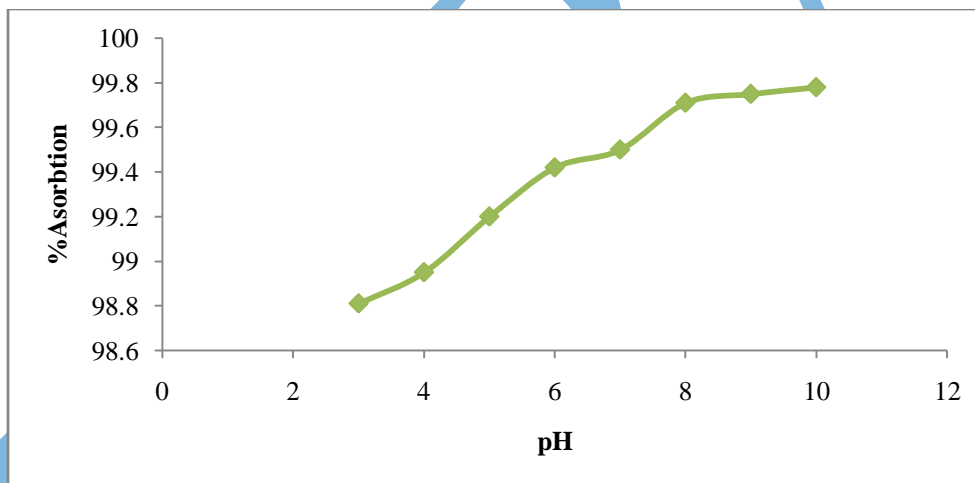


Figure 2: pH effect of Cr⁺³ ions on zirconium oxide (initial concentration = 100ppm)

Effect of temperature on percent adsorption

The temperature has pronounced effect on the percent adsorption of the metal ions, the % adsorption of chromium ion on zirconium oxide surface decreased with increasing temperature, which shows that desorption starts as the temperature increase above 50 °C. The Table 4 and Figure 3 show the percent decrease in the adsorption of chromium on Zirconium oxide.

Table 4: % Adsorption of K⁺ on zirconium oxide at different temperature (initial concentration = 100mg/L)

Temp (°C)	% adsorption of K ⁺
10	99.00
20	98.95
30	98.93
40	98.90
50	98.87

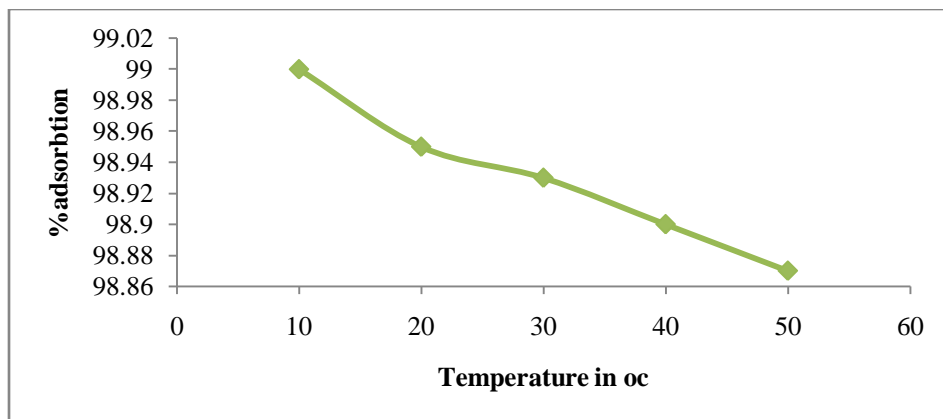


Figure 3: Effect of temperature on adsorption of Cr^{+3} ions on zirconium oxide (initial concentration = 100ppm)

IV. CONCLUSIONS

This study was conducted to assess the effectiveness of the use of zirconium oxide powder as a medium for the adsorption of Cr^{+3} in waste water. Based on the results, the following conclusions were drawn.

The adsorption capacity of zirconium oxide increased with increasing metal ion concentration. The adsorption

capacity of zirconium oxide increasing with increasing pH.

The adsorption capacity of zirconium oxide decreased with increasing temperature.

V. ACKNOWLEDGEMENT

The authors are grateful to the Department of Chemistry, Kohat University of Science & Technology, Kohat, for providing Facilities to conduct research.

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