ASTES

Factors Affecting the Adsorption of Trivalent Chromium Ions by Activated Carbon Prepared from Waste Rubber Tyres

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A R T I C L E   I N F O

A B S T R A C T

Economic gains are generally the outcome of industrialization and consequently urbanization. However, positive fiscal index generates a negative impact on natural environment sources heaving pollutant burden on soil, air and water. Industries throw tones of contaminated water into soil and water bodies without proper treatment and create a potential threat for both living and non-living species. Chromium in trivalent state (Cr^{3+}) is added in water bodies and soil through waste water from tanneries, cooling water systems, chemical and pulp and paper industries. The present research work aims at the preparation of an inexpensive activated carbon prepared from non- degradable waste scrap rubber tyres. The carbon produced from scrap rubber tyres was activated by 5% solution of $BaCl_2$ and 0.4 N solution of HCl and verified by ethylene blue solution. The adsorption capacity of the Tyre activated carbon (TAC) was investigated for different parameters i.e., initial chromium (III) ion concentration, activated carbon dosage, contact/ stirring time and pH. The adsorption capacity of TAC depends on the initial metal ion concentration and the TAC dose. pH of the chromium solution effects the adsorption capacity of TAC due to the formation of tetra hydroxochromate(III) complexes,. The results show that TAC offers a cost effective reclamation process for the removal of Cr^{3+} from effluent waters.

1. Introduction

Industrialization and urbanization at a fast rate, especially in the developed countries, is todays leading need due to rapid population growth and thus directly linked with advancements in economics. High economic gains has its beneficial as well as adverse effects. Industrial progress has intensified pollution problems worldwide. Land, air and water pollution is building up due to inefficient execution of environmental laws. One of the major concerns is water pollution caused by effluents from various industries. The present paper is an extension of the original work that presented the removal of Copper ions (Cu^{2+}) from industrial waste waters by TAC [1].

Economic booms have lifted up many people from agonizing poverty through industrialization. However, this has resulted in serious environmental degradation (China Water Quality Management Policy and Institutional Considerations, World Bank,

2006). Industries use tones of water for various processes and also release large quantities of waste water (loaded with spent chemicals and metallic residues) in the nearby lakes, rivers and canals without suitable treatment. Many areas of the world have now lost access to safe drinking water. It is estimated that 2000 children under the age of five die daily. 90 % of such deaths are linked with diarrheal diseases due to intake of contaminated water and improper sanitation and hygiene conditions. A press release by UNICEF (New York, 22 March 2013) states that 783 million people do not have access to safe drinking water (comprising of China on the top with 119 million, then India, Nigeria and lastly Pakistan at the bottom with 15 million).

Release of chemicals in aquatic environment brings changes in the structure and functional properties of water species [2] and sometimes results in their total extinction. A major concern of today are the heavy metals which are toxic above certain concentration [3-4] and henceforth, a potential threat for the consumers. Severe ecological problems are arising due to the contamination of surface and ground water. Some plant species

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are able to withstand low concentrations of certain metals but generally face eradication at high levels [5]. Mostly heavy metals are carcinogenic and get incorporated in the food chain. Biomagnification and bioaccumulation [6] of heavy metals in the living beings has further aggravated the situation.

Chromium metal possesses three stable valence states i.e., 0, +3 and +6. Dietary Cr^{3+} is an essential trace mineral requirement of human body for the control of glucose metabolism by insulin [7]. is proved to be a potential carcinogen [8-9]. In [10]-[11], the authors have reported that even Cr^{3+}, when taken as supplement, can accumulate in tissues and can bring about structural changes in DNA. A major release of Cr^{3+} is through tanneries and cooling water systems, and from refractory, chemical and metallurgical industrial operations. Cr^{3+} incorporation into the ecosystem and delivery to humans via e.g., vegetables [12] and seepage to the ground water has adversely affected human lives. It is therefore, immensely important to address this pertinent issue which needs strict implementation of Cr^{3+} removal systems from waste waters.

Several methods for the removal harmful ions in water are effective e.g., chemical precipitation, electrolysis, membrane technology, ion exchange etc. and are in common practice by the industries. Adsorption of ions onto a suitable adsorbent is a low cost, effective and easy method for the separation of undesired chemicals. Adsorption [13-14] i.e., physiosoprtion or chemisorption can adequately remove matter in solid, gas or liquid form. Several waste materials are reported to be good adsorbents [15-16]. Activated carbon is especially favored due to its inert nature [17-18]. In this study, activated carbon derived from scrap rubber tyres is used as an adsorbent for the removal of Cr^{3+} from aqueous solutions. The major aim was to test the performance of TAC as the function of adsorbent dose, Cr^{3+} concentration in solution, pH and the contact time. This will be a cost-effective utilization of non-degradable scrap rubber tyres for water purification.

2. Materials and Methods

2.1. Preparation of Activated Carbon from Scrap Rubber Tyre

Scrap rubber tyres were collected from disposal sites. These were cut into small pieces, washed several times with distilled water and dried. Pieces were then crushed and grinded in mortar and pestle. 600gms of the ground rubber tyres was taken in a round bottomed flask fitted with a water condenser. Dry distillated of tyres was done at 450 °C. Three main fractions were obtained i.e., chars, oils plus water mixture and obnoxious gases. The residue chars were heated in a muffle furnace at 800-900 °C for 30 seconds and cooled to room temperature in desiccators. It was then soaked in 5% $BaCl_2$ solution for 12 hours for chemical activation and then filtered. The carbon was firstly washed with HCl (0.4 N) and then several times with distilled water to remove the oxides and soluble impurities. The final residue sample was dried in an oven overnight at 105°C. The dried TAC was sieved and 200 mesh size was selected for Cr^{3+} removal studies.

2.2. Confirmatory Test for the adsorption capacity of TAC.

The efficiency of TAC was tested by Methylene Blue test. 0.2gm of TAC was immersed in 10ml of 1% Methylene blue solution in a 50ml beaker. Same test was performed with commercially available Merck activated carbon for comparison. The absorbance was measured at λ_{max} of 660nm.

The adsorption capacity. *AC* (%) of TAC was calculated using following relationship:

$$AC\ (\%) = \frac{ci - ct}{ci} \times 100$$

Where

Ci = initial concentration of the simulated solution

Ct = The concentration of solution after treatment.

The adsorption capacity (or the removal of Cr^{3+} - %) of TAC was checked on Varian spectrophotometer using an acetylene-air flame and lamp current of 7 mA for Cr^{3+} determination.

2.3. Preparation of Chromium(III) solutions

Chromium sulphate $(Cr_2(SO_4)_3.12H_2O)$ salt was dried in an oven overnight at 50 °C. Stock solution of 1000 ppm was prepared by dissolving 7.70 gms of salt in de-ionized in a measuring flask of 1L. Further dilutions of 50 ppm, 100 ppm & 200 ppm solutions were made from stock solution.

The following tests were performed to check the adsorption capacity of the prepared TAC.

2.4. Effect of TAC dosage on adsorption of chromium (III) ions

Five volumetric flasks of 50 ml capacity were taken. 25 ml of 200 ppm solution of Cr^{+3} ions was poured in each flask. 0.1 gm, 0.2 gm, 0.3 gm, 0.4 gm and 0.5 gm of TAC was added. The solutions were stirred for 3 hours on magnetic stirrer at 600 rpm and then filtered. The concentration of Cr^{3+} left in solution after adsorption tests was checked by Atomic absorption spectrophotometry (AAS).

2.5. Effect of chromium (III) ions concentration on adsorption by the TAC

25 ml of 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm Cr^{3+} solutions were taken in five measuring flasks. 0.1 gm of TAC was added. The solutions were stirred for 3 hrs on magnetic stirrer at 600 rpm and then filtered. The amount of Cr^{3+} remaining in solution in each flask was measured by AAS.

2.6. Effect of contact time on the adsorption capacity of TAC

25 ml of Cr^{3+} solution (200 ppm) was taken in five separate 50 ml volumetric flasks (x5). TAC (0.1 gm) was added to each flask and the solutions were stirred for different time intervals i.e., 1, 2, 3, 4 and 5 hours on magnetic stirrer at 600 rpm. Cr^{3+} remaining in solution after each time interval was checked by AAS.

### 2.7. Effect of solution pH on the adsorption capacity of TAC.

Cr^{3+} solutions (25 ml) were taken in four separate 50 ml volumetric flasks. The pH of solutions was maintained at pH 4, pH 5, pH 7 and pH 10. TAC (0.1gm) was added to each flask and the solutions were stirred for 3 hours at 600 rpm. After the adsorption test each solution was filtered and the Cr^{3+} concentration was checked by AAS.

3. Results & Discussion

Water pollution by the industries have risen to colossal disasters in many parts of the world. The developing countries are facing tremendous ill health effects due to water contamination especially by heavy metals [19-20]. Many living species are eradicated leaving environmental issues that need remediation. This has led the scientists to find new methods and materials for survival of living beings. Adsorption of harmful chemicals and heavy metals is a cheap method for the removal of contaminants. In recent years, several adsorbents and particularly bio adsorbents [21-23] have been investigated to combat pollution arising as a consequence of anthropogenic activities. Rubber tyres are non-biodegradable. These have no use except illegally burned to produce obnoxious fumes or dumped in tones at waste sites. We have made use of waste rubber tyres and converted it to activated carbon for the reclamation of waste water.

The efficiency or the adsorption capacity of the prepared TAC was checked by the Methylene blue test and compared with commercial Merck Activated Carbon (powdered) at λ_{max} of 660 nm. The blank solution showed an absorbance of 2.707. The dye absorbance test showed that TAC had absorbance of 0.053 and the commercial Merck Activated Carbon had absorbance of 0.035. Thus, our prepared TAC showed good absorbance capacity for the dye.

It is envisaged that as the amount of adsorbent is increased, the removal of metal ions should also increase systematically. TAC required to effectively adsorb Cr^{3+} was checked by varying TAC dose for 200 ppm concentration. The results are presented in Figure 1.
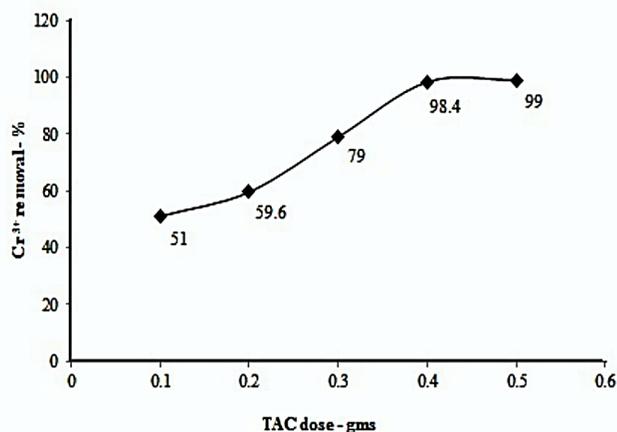
The adsorption percentage of Cr^{3+} (200 ppm) increases with the amount of adsorbent dose. Maximum adsorption of 99 % was observed with 0.5 gm TAC of 200 mesh size at pH 6.5 (nearly neutral) after a contact period of 3 hours held at a stirring speed of 600 rpm. This important parameter has been studied by several researchers before [24-25]. In our earlier work [1], TAC proved to be an effective adsorbent for the removal of Copper (II) ions from industrial waste water. Sharma and Goyal [26] have found strong effect of adsorbent dose on removal of Cr^{3+} from tannery effluents at pH-4 by Aspergillus sp biomass. Recently, Jamil et al

[27] have reported similar dose effect of Pakistani coal derived activated carbon on removal of Cr^{3+} from simulated solutions. The exchangeable sites for the metal ion adsorption increase with the increase in TAC dose and hence, the water is cleaned from the contaminant ions. The distribution coefficient for the TAC dose tests varies in the range of 10.4 to 198. The Gibbs free energy (ΔG)changes from -5.8 KJ/mole through -13.4 KJ/mole telling that Cr^{3+} removal by adsorption is a favorable process. We selected TAC (mesh-200) dose of 0.1gms and Cr^{3+} concentration of 200 ppm for further experimentation so that variations can be studied more thoroughly.

The effect of initial metal ion concentration is shown in Figure 2.
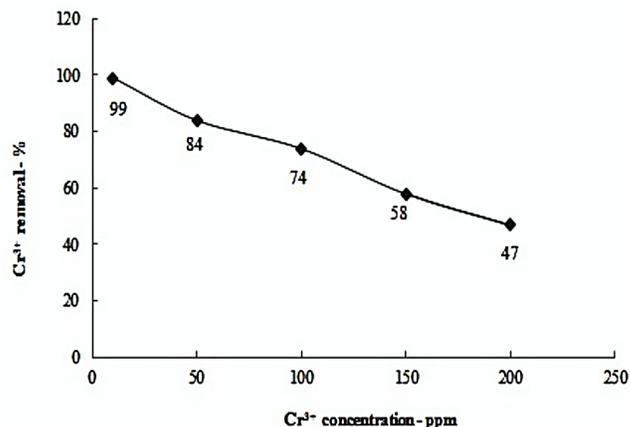
The removal of metal ions from aqueous solutions by adsorption is highly dependent on the initial metal ion concentration in solution [28-29]. The adsorption efficiency of adsorbents is applicable in a specific range of concentrations as the active site may be filled above certain concentrations. Figure 2 shows that the adsorption decreased when the concentration of the metal ions increased. Maximum adsorption of 99% was observed at low concentration of Cr^{3+} ions i.e., 10 ppm and linearly declined as the initial Cr^{3+} concentration increased. Adsorption reduced to 47% with 0.1gms of TAC at 6.2 pH at contact time of 3 hours. TAC amount is the limiting factor. The exchangeable sites with a low dose amount of 0.1gms became saturated with Cr^{3+} ions at 10 ppm concentration. The site coverage is reached and equilibrium is established. At higher initial concentrations of Cr^{3+} ions, the adsorption percentage decreases due to low availability of active sites. We observed the surface charge interaction phenomenon in absence of diffusion.

The contact time of adsorbent with the metal ion solution is an important factor that effects the adsorption capacity [30, 31]. Cr^{3+} absorption by 0.1 gm TAC dose as the function contact time is shown in Figure 3.

The results show that as the contact time of TAC with Cr^{3+} solution is increased, the removal of Cr^{3+} also increases. Under constant stirring conditions, maximum adsorption of Cr^{3+} (50%) was observed in 3 hours. After 3 hours, no significant change in Cr^{3+} removal is observed. Thus, 3 hours was found sufficient for achieving equilibrium.
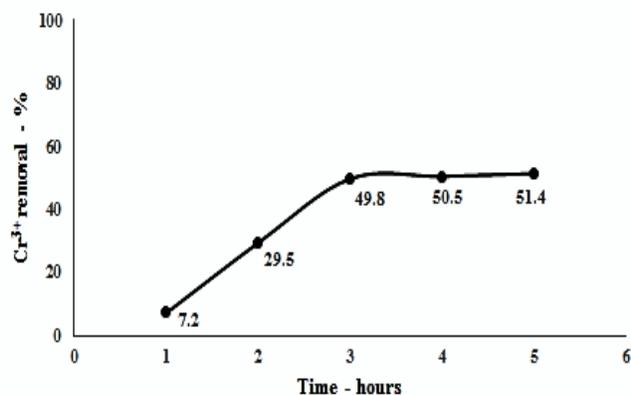
Figure.3. Effect of contact time on Cr (III) adsorption (initial Cr^{3+} concentration: 200 ppm, TAC dose: 0.1g, pH - 6, stirring speed: 600rpm)

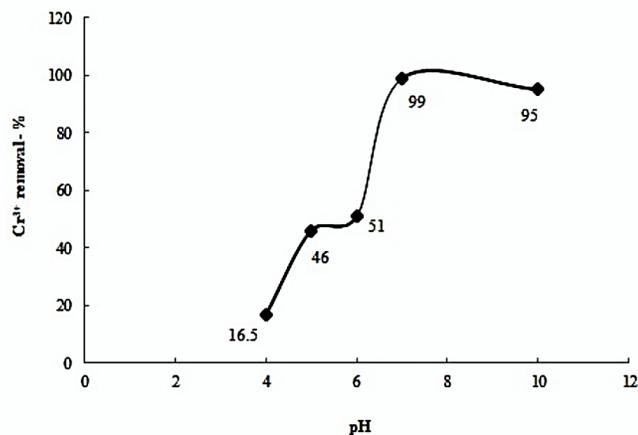The effect of pH on adsorption process is presented in Figure 4.

Figure.4. Effect of solution pH on Cr (III) adsorption (initial Cr^{3+} concentration 200ppm, contact time: 3 hours, activated carbon dose: 0.1g, stirring speed: 600rpm)

The removal of metal ions i.e., the absorptive capacity of adsorbents is dependent upon optimal pH level of the metal ions solution (32-33). In acidic medium (pH-4), Cr^{3+} is present as mononuclear hydrated ion. Figure 3 shows that the adsorption efficiency of TAC for Cr^{3+} is very low i.e., only 16.5%. At acidic pH, the hydronium (H^+) ions affiliation to the adsorbents surface is responsible for TACs' poor adsorption efficiency. The adsorption efficiency of TAC for Cr^{3+} increases with an increase in pH till pH-5 to 46 %. Deprotonation of metal binding sites on TAC also occurs when the solution pH increases. The Cr^{3+} ions are attracted to the vacant sites and hence, higher adsorption is observed. Decrease in positive charge at TAC removes repulsion and hence, improves the attraction of Cr^{3+} ions for active adsorption. Lyubchik et al. [34] have identified carboxylic groups on surface of activated carbons for enhancement in removal of Cr^{3+} at initial solution pH between 2 till 4. Weak change in adsorption occurs between pH 5 through pH 6. At this pH, Cr^{3+} precipitates as hydrated $Cr(OH)_3$. As the pH rises, solubility of chromium (III) increases. Apparently, adsorption of the Cr^{3+} ions is maximum at pH 7 i.e., 99% which is close to 95% adsorption at

pH -10. At alkaline pH, adsorption efficiency is disturbed due to the precipitation of Cr^{3+} as tetra hydroxochromate(III) complexes, $Cr(OH)_4^-$ [35]. Cu^{2+} [1] go into hydroxide formation at high pH. Precipitation is not as effective as adsorption as the separation of precipitates from water is cumbersome. The adsorption efficiency may increase at acidic pH with that activated carbon which has negatively charged surface. Dai, Ren and Tao [36] used solution pH for distinction between Cr (VI) and Cr^{3+} adsorption on chemically modified Chitosan. The adsorption efficiency of Cr(VI) was maximum i.e., 97% at pH 4.0, whereas the adsorption efficiency of Cr(III) was 5%. We have also observed very weak adsorption of Cr^{3+} ions i.e., 16.5 % at pH-4.

4. Conclusions

TAC is an effective low cost adsorbent for the removal of Cr^{3+} and Cu^{2+}ions. It offers treatment of impaired water at reduced energy and time consumption. The inert nature of TAC secures its reliability versus biomaterials which degrade over long time exposures. TAC almost completely removes Cr^{3+} ions from solutions when the metal ions are present in low concentration at pH 5.5. In higher alkaline medium, tetra hydroxo-Cr(III) complexes formation increases.

Conflict of Interest

The authors declare no conflict of interest.

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