APPLICATION OF A NOVEL ADSORBENT- AIRCRAFT TYRE RUBBER ASH FOR THE REMOVAL OF CHROMIUM FROM WASTEWATERS

Lakshmi Adathodi[1,*], Raja Murugadoss J.[1] and Kalyani Gaddam[2]

[1]Department of Civil Engineering, GMR Institute of Technology,
Rajam-532127, (Andhra Pradesh) India
[2]Department of Chemical Engineering, GMR Institute of Technology,
Rajam-532127, (Andhra Pradesh) India
*E-mail: lakshmi.adathodi@gmail.com

ABSTRACT

The eco-friendly and cost-effective technique of using tyre rubber waste for the removal of harmful toxic metals from wastewater will contribute a lot to the industry as well as the humanity from the environmental perspective. In the present work, an attempt has been made using aircraft tyre rubber waste carbon to remove the heavy metal chromium which is added to the water bodies through wastewater from various manufacturing industries. The batch study was performed to determine the removal efficiency by testing the effect of parameters such as contact time, dosage, initial concentration, pH of the solution and temperature. The amount of chromium ions removed from solution decreased rapidly from pH 3 to pH 9. Increasing the adsorbent dose increased the percentage removal of chromium from 14.94 % to 92.24 %. The removal efficiency of chromium using aircraft tyre rubber waste carbon was relatively fast (equilibrium time of 60 minutes). The removal efficiency of chromium decreased from 59.79% to 49.02% with increasing concentration. The removal efficiency increased with an increase in temperature as well as an increase in dosage. The prepared adsorbent was characterized using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometry (EDS / EDX) and X-ray diffraction (XRD) analysis to investigate the distinctive features of aircraft tyre rubber waste carbon. The results show that ATRWC has an excellent ability to remove chromium from the wastewaters.

Keywords: Aircraft tyre rubber waste carbon, Adsorption, Aqueous solution, Removal efficiency, Chromium

INTRODUCTION

In the recent era, the fast-moving world increased the growth of automobile industry which has boosted the tyre production which is being considered as the most problematic source for the generation of solid waste, due to the large volume produced and their durability.[1] Globalization has contributed to the aviation industry to extend its passenger services connecting all possible places across the world. As a result, the frequency of landing and take-off of large aircraft has tremendously increased. Though the passenger services significantly increased on one side, it created a serious threat on the other side with more deposition of rubber at the time of landing and take-off.[2] besides the economic growth, the solid waste generated by these tyres lead to high environmental pollution. Most of the tyre rubber waste is recycled to obtain value-added products for fuels, roads etc., but similar quantity is still discarded without proper treatment.[3,22] The disposal of tyre rubber waste also involves expensive, dangerous transporting and storing facilities.[4,23] Most of the tyre rubber waste is being sent to landfills or the open dumps, which raises a concern for the environmental pollution and social unrest.[5,21] The scientific research has grown to recycle and reuse the tyre rubber waste from a few decades and one possible application is to prepare activated carbon for the removal of harmful pollutants from wastewater. The increase in the manufacturing industries has led to the rapid release of toxic metals into the aquatic ecosystems, thereby

posing a hazard to the human health and the environment. The increased pollutants are found well above the threshold limits in the aquatic environment creating a great concern towards the protection of the ecosystem.[6,7] Chromium is a well-known legendary pollutant being released from the manufacturing industries like tanneries, mining, cement ceramics and glass industries, manufacture of catalysts, fungicides, photography, pigments and paints, electroplating, production of steel and other metal alloys, photographic material and corrosive paints, chrome plating, etc.,[8,9] Chromium is released into the environment not only from natural sources but also from human activities. Chromium removal is of much concern because of its toxicity.

Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes inevitable. Adsorption is one of the most versatile and widely used techniques for the removal of toxic metals from the aqueous solutions. From more than three decades, activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to make it possible for the potable usage.[10,11] A wide variety of materials such as chitosan, granular red mud[12], sugar beet pulp[13], rice husk[14], rice bran[15,16], activated carbon[17], Zeolite by Stylianou, Mimusops elengi[18], sawdust, cocoa shells by Meunier, Sargassum[19], Pithophora Cleveana Wittrock[20] and leaves[25] are examples of low-cost adsorbents used for the removal of heavy metals. The present study aims to assess the applicability of activated carbon derived from the aircraft tyre rubber waste for the removal of chromium from wastewaters to investigate the effect of operating parameters on the adsorption process. The parameters studied include contact time, initial chromium concentration, adsorbent dosage, initial solution pH and temperature. The results of the analysis could provide economical and effective technical support to full-scale industrial wastewater treatment plants with the utilization of aircraft tyre rubber waste.

EXPERIMENTAL

Reagents and Chemicals
The basic material used in the present study was sieved residual aircraft tyre rubber waste obtained from runways. Hydrogen peroxide (H_2O_2), Potassium Dichromate ($K_2Cr_2O_7$), Nitric Acid (HNO_3) and other chemical reagents were obtained from different standard manufacturing industries. A metal solution of Chromium with different concentrations was prepared by dissolving the appropriate amount of Potassium Dichromate ($K_2Cr_2O_7$) in distilled water. 0.1 N NaOH and HCl solutions were used for pH adjustment. In order to prevent metal contamination from laboratory glassware, glassware was kept overnight in a 10 % (v/v) Nitric Acid (HNO_3) solution. All commercial chemical reagents were handled very carefully and storage was also in compliance with the recommendations. A digital pH meter (Orion make) was used for all pH measurements. A high precision electrical balance was used for weighing. Continuous mixing was provided during the experimental period with a constant agitation speed for better mass transfer with a high interfacial area of contact.

Instrumentation
   i.   Orbital shaker (REMI-CIS-24plus model): to agitate the metal solutions with adsorbents
   ii.   Muffle Furnace (3.5 KW, 230V, 50Hz): to activate the tyre rubber powder
   iii.   pH Meter with a glass electrode (335A, Systronics, Ahmadabad, S. No.: 7898): to measure the pH of the metal solutions
   iv.   Filter paper (Whatman-42): to filter the metal solutions and the adsorbent mixture
   v.   Analytical Balance (Shimadzu, AUX220): to weigh the adsorbents
   vi.   UV-Visible Spectro photometer (Double beam): to determine the absorption of light from a sample and can be used as a detector for High-performance liquid chromatography (HPLC)

Preparation of Adsorbent
Activated carbon was prepared from aircraft tyre rubber waste via carbonization, chemical treatment, and steam activation. The rubber waste powder was cleaned, thoroughly washed with deionized water, and then dried in an oven at 100°C for 4 h. For carbonization, the dried material was heated to approximately 120°C for 24 h. This was followed by treatment with 30 % hydrogen peroxide (H_2O_2) solution for 2h to oxidize adhering organic impurities. The material was washed with deionized water and dried in a

vacuum oven at 60°C for 24h. The dried material was activated to 500°C for 2 h (N_2 flow 0 225 mL min⁻¹). Then, it was removed from the furnace and cooled in a desiccator. The material was then treated with 4 M nitric acid solution to remove the ash content and was then washed with deionized water. The product was finally dried in an oven at 120°C for 24h.

Characteristics of Adsorbent Material

The physical properties and chemical composition of the Aircraft tyre rubber are presented below. The morphological characteristics of the adsorbent were evaluated by using a Phillips XL30 SEM, and the chemical composition was justified by performing EDS / EDX and XRD analysis.
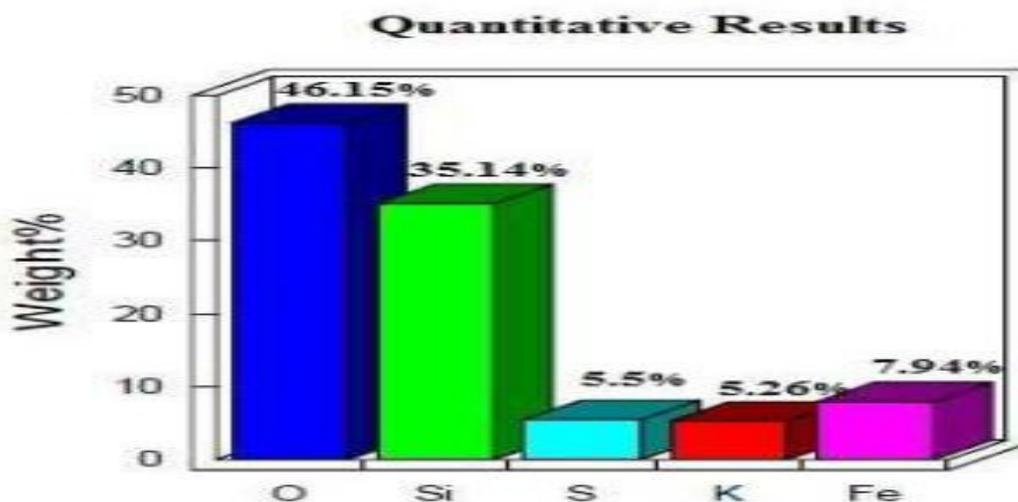

Fig.-1: Chemical Analysis of Waste Tire Rubber Ash

Batch Adsorption Experimental Studies

The adsorption studies were conducted in exploratory conditions of various effective process parameters of pH 3-9, contact time 60-120 min, metal ion concentration ranges 50ppm-150ppm, the dosage of the adsorbent 0.25g-0.75g and the temperature 25 °C-35 °C. The agitation speed of 350 rpm was kept constant in the orbital shaker with the suitable time interims. The mixed adsorbent solutions were taken out and filtered by Watmann filter paper and analyzed for metal ion concentration in a UV-Visible Spectro-photometer (Double beam). Batch experiments were conducted by changing the parameters like contact time, initial chromium concentration, adsorbent dosage, initial solution pH and temperature by utilizing orbital shaker from 303K - 323K. Samples were analyzed by UV-Visible Spectro-photometer.

RESULTS AND DISCUSSION

Effect of pH

It is well known that the removal of heavy metals by adsorbent depends on the pH of the initial solution. Therefore, in order to establish the effect of pH on the adsorption of chromium ions, the batch equilibrium studies were carried out at different pH values. The pH range was chosen 3-9. The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH and prepared tyre rubber adsorbent were added to 100 ml of solution in 250 ml flasks. The adsorbent was thoroughly mixed with the help of magnetic shaker for 90 minutes and the adsorbent mixture was filtered using Whatman filter paper. The prepared standard solutions along with the filtered adsorbent mixture were tested for the chromium. The progress of adsorption was assessed by determining the residual concentration of Cr in the supernatant by the UV-Vis Spectrophotometer. Figure-2 shows the amount of chromium ions removed from aqueous solution as a function of pH at a Cr concentration of 100 mg/L. The amount of chromium ions removed from solution decreases rapidly from pH 3 to pH 9. At pH 3, 90.30% of Cr ion was removed, while at pH 7, 8.16% of Cr ion was removed and at pH 9, the amount of chromium ion removed from the solution by the aircraft tyre rubber adsorbent steadily decreased to 5.93%.[26]
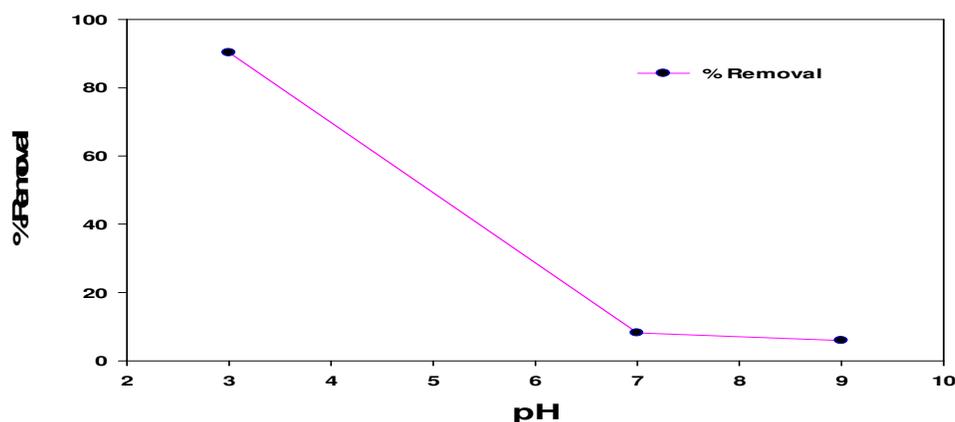
Fig.-2: Effect of pH on the Removal of Chromium by Aircraft Tyre Rubber Carbon: 100 mL of solution, 0.5 g/100 ml of Adsorbent, 100ppm Concentration,Temperature 30ºC, time 90 min, pH 3, 7 and 9

Effect of Adsorbent Dose

To determine the capacity of an adsorbent for a given initial concentration of metal ion solution, dosage study is an important parameter which determines the capacity of an adsorbent. The effect of adsorbent dose on the percent removal of chromium at the concentration of 100 ppm is shown in below Fig.3. From the Fig.2, it can be observed that increasing the adsorbent dose increased the percent removal of chromium from 14.94 % up to 92.24 % with the required optimum dose of 0.75 g/100 ml of chromium solution. As expected, the removal efficiency increased with increasing the adsorbent dose for a given initial metal concentration, because, for a fixed initial adsorbate concentration, increasing adsorbent dose provides a greater surface area or more adsorption sites. Further, it can be attributed to the binding of metal ions onto the surface functional groups present on the Aircraft tyre rubber carbon. On the other hand, when the rubber carbon dose increased more than the limit, the adsorption capacity (the amount adsorbed per unit mass of adsorbent) decreased. The decrease in adsorption capacity with an increase in the adsorbent dose is mainly due to the increase of free adsorption sites in the adsorption reaction.
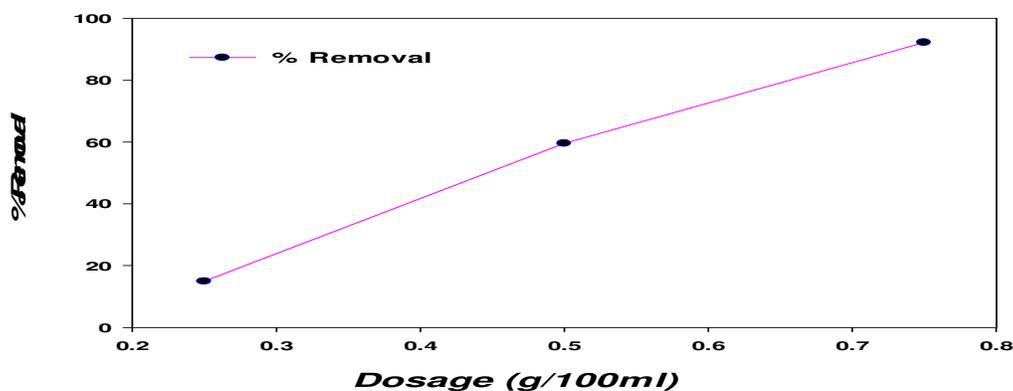

Fig.-3: Effect of Adsorbent Dosage on the Removal of Chromium by Aircraft Tyre Rubber Carbon: 100 mL of Solution, pH 3, 100ppm Concentration, Temperature 30ºC, Time 90 min, and 0.25, 0.5 and 0.75 g/100 ml of Adsorbent.

Effect of Contact Time on the Removal of Chromium

The effect of contact time for the Cr removal at the condition of 0.5 g/100 ml solution of the adsorbent, optimal pH 3.0, the initial concentration of 100 ppm with a temperature of 30 ºC and the contact time of 60 min. As indicated in Fig.4. the Cr removal efficiency was decreased slowly up to 90 min and then it reached very lower level right after 60 min. The sharp decrease in the removal efficiency may be due to the existence of enormous vacant active sites on the adsorbent surface. However, by raising the contact

time the availability of Cr ions to the active sites on the adsorbent surface is limited, which results in low removal efficiency. In a further related study,[27] reported that the adsorption of Cr on nano-carbonate hydroxyl apatite reached the equilibrium state at 90 min at different concentrations of Cr. Since 90 min is more than the optimal time obtained in the present study, it can be noted that the Aircraft tyre rubber carbon has higher adsorption rate than nano-carbonate hydroxyl apatite.
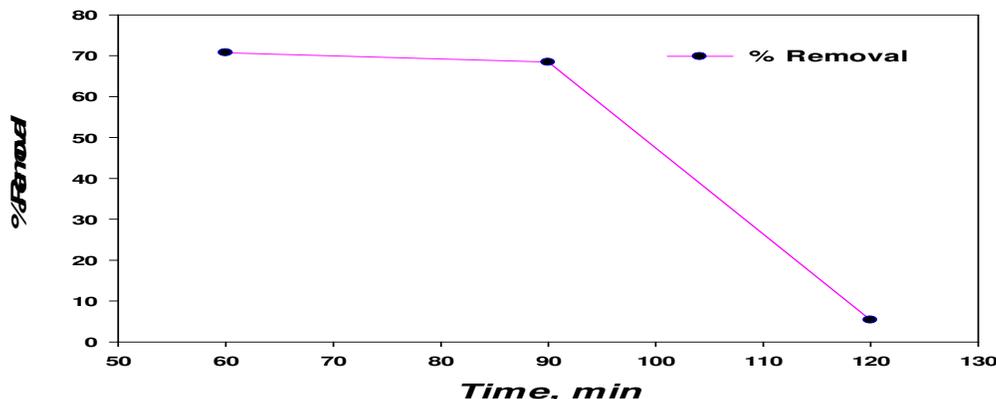

Fig.-4: Effect of Contact Time for the Removal of Chromium by Aircraft Tyre Rubber Carbon: 100 mL of Solution, pH 3, 100ppm Concentration, Temperature 30ºC, Contact time 60min, 90min and 120min.

Effect of Concentration of Solution
The concentration of the solution changes the percent removal of metal ions from aqueous solution. The effect of concentration was calculated by changing the concentration of the solution as 50 ppm, 100 ppm and 150ppm at 30 ºC with the contact time of 90 min, pH 3 and adsorbent dosage of 0.5g/100 ml of solution. Results mentioned in the Fig.5. Explained that the removal efficiency decreased with increasing the concentration of the metal ion solution.[27]
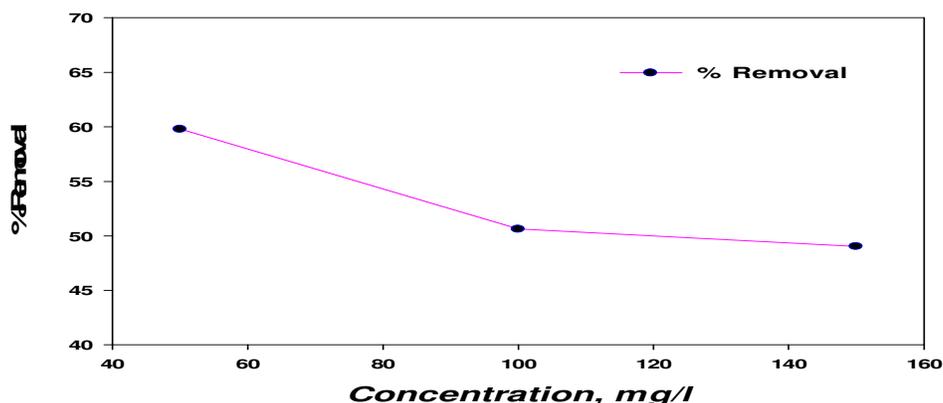

Fig.-5: Effect of Concentration for the Removal of Chromium by Aircraft Tyre Rubber carbon: 100 mL of Solution, pH 3, Temperature 30ºC, Contact time 90min, Concentration 50ppm, 100ppm and 150ppm.

Effect of Temperature on Removal of Chromium
To determine whether the ongoing adsorption process was endothermic or exothermic in nature, chromium adsorption studies using Aircraft tyre rubber carbon were carried out between 25 ºC -35 ºC for the initial feed concentration and at a constant adsorbent dose of 0.5 g/ 100 ml solution. It can be observed from Fig.6.that the adsorption of chromium ions increased when the temperature was increased up to a certain temperature i.e., at 25 ºC the amount of Cr ion removed was 9.34 %, whereas, at 30 ºC, 79.47% of Cr ion was removed by rubber carbon for an initial concentration of 100 ppm. It can be seen from the figure that, initially, the percentage removal increased sharply with the increase in temperature, but beyond a certain value of 30 ºC, the percentage removal decreased to a minimum value. These results

showed that the sorption was endothermic in nature upto a certain point.[27] The increased sorption with the rise of temperature may be diffusion controlled, which is an endothermic process, i.e., the rise in temperature favors the sorbate transport within the pores of sorbent.
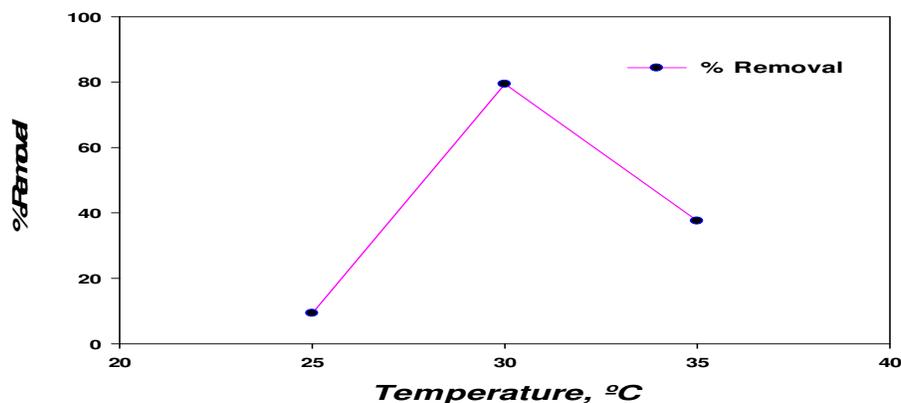

Fig.-6: Effect of Temperature for the Removal of Chromium by Aircraft Tyre Rubber Carbon: 100 mL of Solution, pH 3, Contact time 90min, Concentration 100ppm, Temperature 25ºC, 30ºC and 35ºC

Effect of Optimum Conditions
Functionalized activated Carbon derived from Aircraft tyre rubber was investigated for the adsorption of chromium from aqueous solutions. It was demonstrated in this study that aircraft tyre rubber carbon could be used as an effective adsorbent for Cr and optimum conditions were found. The equilibrium time is 60 min for the adsorbent having a concentration of 50 ppm. The maximum adsorption takes place at the pH of 3.0 with the temperature of 30 ºC.
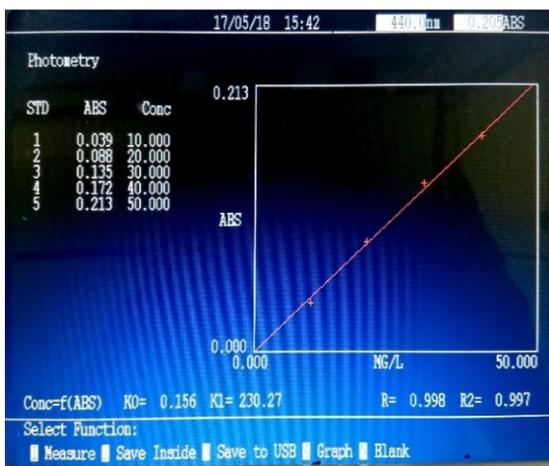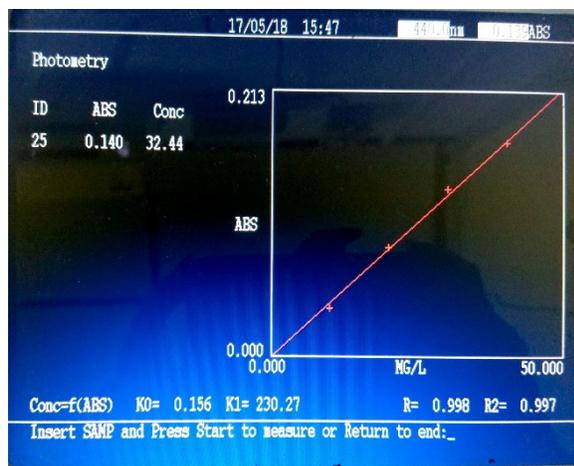

Fig.-7: Concentration for Standard Solution   Fig.-8: Optimum Removal Efficiency for Cr Metal Ion

Table-1

Parameter	Optimum Point	Cr removal Efficiency %
pH	3.0	90.30
Dosage	0.75g	92.24
Concentration	50ppm	59.79
Contact time	60 minutes	70.75
Temperature	30 ºC	79.47

CONCLUSION

In the present study, the removal efficiency of chromium from wastewaters using ATRWC was investigated in a batch system. Characterization using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometry (EDS / EDX) and X-ray diffraction (XRD) was done to confirm the chemicals present in the prepared ATRWC. The following conclusions can be drawn.

The resulted removal efficiency by setting the obtained optimum parameters was 67.56%. The obtained result can be stated as a good investigation for the possibility of the utilizing the ATRWC as a low cost adsorbent for removal of chromium from wastewaters.

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