

Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste

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Abstract

Chromium is commonly found in huge quantities in tannery wastewaters. For this reason, the removal and recovery of the chromium content of tannery wastewaters is crucial for environmental protection and economic reasons. Removal and recovery of chromium were carried out by using low-cost potential adsorbents. For this purpose three types of activated carbon; C1, the waste generated from sugar industry as waste products and the others (C2, C3) are commercial granular activated carbon, were used. The adsorption process and extent of adsorption are dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental condition. The effect of pH, particle size and different adsorbent on the adsorption isotherm of Cr(III) was studied in batch system. The sorption data fitted well with Langmuir adsorption model. The efficiencies of activated carbon for the removal of Cr(III) were found to be 98.86, 98.6 and 93 % for C1, C2 and C3, respectively. The order of selectivity is C1 > C2 > C3 for removal of Cr(III) from tannery wastewater. Carbon "C1" of the highest surface area (520.66 m²/g) and calcium content (333.3 mg/l) has the highest adsorptive capacity for removal of Cr(III). The results revealed that the trivalent chromium is significantly adsorbed on activated carbon collected from sugar industry as waste products and the method could be used economically as an efficient technique for removal of Cr(III) and purification of tannery wastewaters.

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1. Introduction

The presence of trivalent and hexavalent chromium in the environment is the case of many well-known toxic effects [1]. The main sources of chromium pollution are mining, leather tanning, cement industries, uses in dyes, electroplating, production of steel and other metal alloys, photographic material and corrosive paints [2,3].

The tanning process is one of the largest pollutants all over the world. The total number of tanneries in Egypt is more than 300, of which more than 85% adopt the chromium tanning process because of its processing speed, low costs, light color of leather and greater stability of the resulting leather [4]. The function of chromium salts in tanning processes is to form, through complexation with the polypeptide collagen components of leather,

a protective layer, which prevents the penetration of water inside the leather pores avoiding putrefaction. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs in two forms; trivalent Cr³⁺ and hexavalent Cr⁶⁺. The hexavalent form is 500 times more toxic than the trivalent [5].

Conservative technologies for metal control have an increasing interest, as they able to remove pollutants and reuse valuable by-products resulting from the wastes and/or side streams from manufacturing processes. Removal of metals from wastewater is achieved principally by the application of several processes such as adsorption [6], sedimentation [7] electrochemical processes [8,9], ion exchange [10], biological operations [11], cementation [12], coagulation/flocculation [13], filtration and membrane processes [14,15], chemical precipitation and solvent extraction [16,17].

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Cost-effective alternative technologies or adsorbents for the treatment of metal-containing wastewaters are needed. Activated carbons are more effective in the removal of heavy metals due to some specific characteristics that enhance the use of activated carbon for the removal of contaminants including heavy metals from water supplies and wastewater [18]. Natural materials that are available in large quantities or certain waste products from industrial operations [19–21] and agricultural by-products [22–24], may have potential as inexpensive adsorbents. Generally, adsorbents can be assumed as low cost if they require little processing, are abundant in nature, or are a by-product or waste material from another industry [25]. Low cost activated carbon adsorption is an attractive method because its cost and possible regeneration of the carbon.

Many studies have been investigated the adsorption of hexavalent chromium on activated carbon [26–30]. Adsorption of hexavalent chromium on activated carbon was reported to be considerable at pH 5–6 and highly dependent upon pH. Huang and Wu [27,28] and Leyva-Raoms et al. [30,31] found that Cr(VI) is adsorbed in the form of the complex bichromate, HCrO_4^- at pH values below 6, whereas activated carbon catalyzes the reduction of Cr(VI) to Cr(III). Few studies were published for adsorption of Cr(III) on activated carbon. They reported a maximum adsorption capacity at pH 5 and the adsorption of Cr(III) on activated carbon can be fitted to the Langmuir isotherm and that the adsorption is irreversible [28,31].

The present investigation is devoted to study the removal and recovery of chromium(III) from tannery wastewater by using low cost activated carbon as waste from sugar industry, namely C1. This industrial by-product is available in large amount in sugar refinery factories in Egypt and also in many other countries in the world. To our knowledge, this sugar waste does not find any economic application and represents a solid pollutant to the environment.

In this study, removal and recovery of chromium with activated carbon were investigated. The effects of pH, particle size and characteristics of activated carbons on the adsorption isotherm were studied. Therefore, our approach is to study the chromium removal efficiency by using low-cost adsorbent materials under variable pH, particle size, and different type of activated carbons in order to remove the hazardous chromium from tanning wastewater and recover Cr(III) for further recycling, as well evaluate the feasibility of these adsorbent for removing Cr(III).

2. Materials and methods

2.1. Adsorbent

Three low cost activated carbons were selected to use in this study; these referred as C1, C2 and C3. C1, a waste material was collected from Hawamdiah sugar refinery company, El-Hawamdiah, Egypt. C1 is used in very large tonnages in the decolorization and refining of sugar. The adsorbent is the carbonaceous residue obtained as a result of the destructive distillation of bones. More detailed about the composition, methods of preparation and regeneration are listed in reference [32].

Table 1

Characteristics of raw tannery wastewater from tanning company Misr El-Kadima, Cairo, Egypt

Parameters	Effluent quality
pH	3.54
Temperature (°C)	28
Total chromium (mg/l)	5500
Copper (mg/l)	1.92
Lead (mg/l)	1.21
Zinc (mg/l)	1.98
Chloride (mg/l)	27456
Sulfate (mg/l)	18580
Total hardness (mg/l as CaCO_3)	975
Total dissolved substances (mg/l)	95000
Acidity (mg/l as CaCO_3)	8790.5
Biochemical oxygen demand (mg/l O_2)	197.5
Chemical oxygen demand (mg/l O_2)	2625.5
Dissolved oxygen (mg/l O_2)	7.2
Tannin (mg/l as tannic acid)	9.2
Ammonia (mg/l nitrogen)	325
Nitrate (mg/l nitrogen)	1.07
Calcium (mg/l as CaCO_3)	920
Magnesium (mg/l as CaCO_3)	55
Turbidity (NTU)	110
Sulfite (mg/l)	1.68

While, C2 and C3 were granular activated carbon (commercial grade). The activated carbon was sieved to varying sizes ranging from 45 to 500 μm , washed repeatedly with double distilled water and dried in an oven at 110 °C for 24 h and then stored in desiccators until used.

2.2. Adsorbate

The wastewater tested in this investigation was obtained from main drain of tanning company in Misr El-Kadima area. The various characteristics of tannery wastewater were shown in Table 1.

2.3. Adsorption studies

Adsorption isotherm data were obtained in an experimental batch adsorber. Accurately weighed masses of carbon C1, C2, and C3 were separately placed in 250 ml glass bottles. One hundred millilitres of the adsorbate solution (tannery wastewater) were added to each bottle. The isotherm bottles were placed in a rotary shaker (Burrel, wrist action shaker, model 75, made in USA) to facilitate mixing and allowed to equilibrate for a period of 3 h. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The first 5 ml of the filtered samples were discarded before samples were taken for analysis in order to minimize the effect of any adsorption of the adsorbates that may occur on the filter membrane.

The chromium in solution and that adsorbed was measured. The amount of Cr(III) adsorbed was determined by mass balances according to the following equation:

$$\% \text{Removal of Cr} = \frac{C_{\text{Initial}} - C_{\text{Final}}}{C_{\text{Initial}}} \times 100 \quad (1)$$

Speciation was done in working pH with MINTEQA2 version 3.11 speciation working programme. MINTEQA2 is a chemical equilibrium modeling system for water chemistry calculations, chemical speciation, titration curves, ion balance, aquatic chemistry, mineral equilibria, solubility diagrams, pH calculations, redox (oxidation-reduction), corrosion calculations, environmental chemistry, ion adsorption, thermodynamic calculations in aqueous systems and much more. The parameters affecting the adsorption process such as adsorbent characteristics, particle size and pH were studied. pH of the solution was adjusted using 0.01N HCl and 0.01N NaOH solution. All the experiments were done at the room temperature (25 ± 0.5).

2.4. Determination of chromium

All chemicals used for preparing chromium standards and reagent solutions for analysis of chromium(VI) were analytical reagent grade and de-ionized water were used.

In the determination of Cr concentration by UV–vis spectrometric method, Cr(III) is converted to Cr(VI) using permanganate and 30% H_2O_2 . The Cr(III) is oxidized to $Cr_2O_7^{2-}$ (dichromate) with $KMnO_4$ and determined colorimetrically using 1,5-diphenylcarbazide to form a purple-violet colored complex [33]. The absorbance of the colored complex was measured in a double beam spectrophotometer (Perkin-Elmer, Lambda 3 UV–vis spectrophotometer), at a wavelength of 540 nm, and chromium concentration of tested samples was determined by a calibration curve prepared using standard solutions of concentrations of Cr(VI) between 0.15 and 0.7 mg/l.

2.4.1. Detailed procedure

One millilitre of H_2SO_4 was added to solution and Cr(III) was oxidized to Cr(VI) by adding $KMnO_4$ and H_2O_2 . The solution was boiled for 20 min to complete the oxidation of Cr(III) to Cr(VI) and to decompose the excess of peroxide and permanganate was destroyed by adding Sod. Azide (NaN_3) and then allowed to cool down. Adding 1 ml of sulfuric acid (1 + 9) and 1 ml of 1,5-diphenyl carbazide (DPC) (250 mg in 50 ml acetone) and subsequent dilution with de-ionized water to 25 ml of volumetric flask.

We avoid excess of sulfuric acid due to the increase in sulfate concentration exhibiting its forming complex with Cr(III) and inhibiting the oxidation of free Cr(III) by permanganate.

2.4.2. Detailed conversion

Color formation is based on the reaction of $Cr_2O_7^{2-}$ with 1,5-diphenyl carbazide (DPC) in an acidic solution. The $Cr_2O_7^{2-}$ is reduced to Cr(III) by the DPC, which is, at the same time, oxidized to 1,5-diphenyl carbazone forming a red-violet complex with the Cr(III).

Also, we can observe the conversion of Cr(III) to Cr(VI) by color change from green to yellow. This method is effective for Cr^{6+} in concentration ≥ 0.05 mg/l.

Table 2
Characteristics of activated carbons

Carbon characteristics	C1	C2	C3
Surface area (m^2/g)	520.66	359.28	111.34
Bulk density (g/cm^3)	1.933	–	–
Apparent density (g/cm^3)	2.72	–	–
Pore volume (ml/g)	0.032	–	–
Magnesium content (ppm)	0.79	2.67	0.25
Calcium content (mg/l) (ppm)	333.3	0.47	2.57
Chloride (mg/l)	Traces	Traces	Nil
Sulfur	Traces	Traces	Traces
Nitrogen	Nil	Traces	Traces

3. Results and discussion

3.1. Characteristics of adsorbents

The various chemical and physical characteristics of the three types of carbon are represented in Table 2. It is evident from the physical properties of the adsorbents that the surface area of C1 is higher than C2 and C3. Thus, it is expected that the adsorption of Cr(III) will be maximum on C1 than C2 and C3. Also, C1 possess high content of Ca^{2+} , which increase adsorption of Cr(III) from solutions and these agree with that in the literature [34].

The IR spectra of C1 indicates three absorption bands at 3432.67, 2015.25, 713.53–1450.21 cm^{-1} due to the presence of OH^- , CO, and CO_3^{2-} groups, respectively, two absorption bands at 1035.6 cm^{-1} and 603.61 cm^{-1} due to the presence of sulfate and two absorption bands at 565.04 cm^{-1} and 873.60 cm^{-1} attributed to the presence of (C-Br) and (C-Cl), respectively. On the other hand, two granular activated carbons C2 and C3 have no absorption spectra in IR region, this apparently due to the absence of surface functional groups. Clearly, C1 has the highest surface area and many surface functional groups.

3.2. Adsorption isotherms

The adsorption isotherms of trivalent chromium at different conditions of pH, particle size, and characteristics of activated carbon are shown in Figs. 1 and 3 and 4. Experimental data were fitted to Langmuir and Freundlich models. The isotherm parameters were calculated using the least squares method that optimization method based on the Rosenbreck algorithm. Since the average percent deviation of the Langmuir isotherm was lower than the Freundlich isotherm, the Langmuir isotherm was used for consistency. The Langmuir isotherm is represented mathematically as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

where C_e is equilibrium concentration of Cr(III) in solution (mg/dm^3); K_L , the parameter of the Langmuir isotherm ($dm^3 g^{-1}$); a_L , the parameter of the Langmuir isotherm ($dm^3 mg^{-1}$); q_e , the mass of Cr(III) adsorbed ($mg g^{-1}$). Values of the Langmuir constants are given in Table 3.

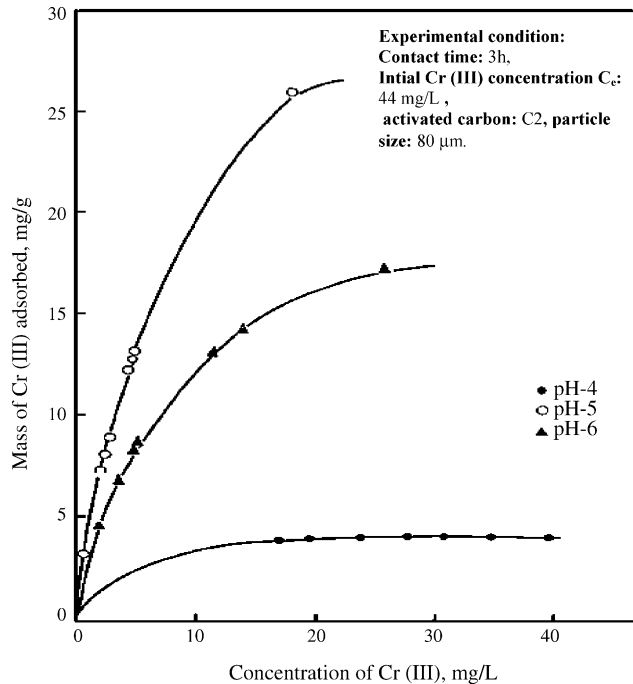


Fig. 1. Adsorption isotherm of Cr(III) onto granular activated carbon (effect of pH).

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R [35], which describes the type of isotherm and is defined by the equation:

$$R = \frac{1}{1 + a_L C_0} \quad (3)$$

where a_L is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. C_0 is the initial concentration of Cr(III).

If,

- $R > 1$ unfavorable
- $R = 1$ linear
- $0 < R < 1$ favorable
- $R = 0$ irreversible

Table 3
The values of the parameters in the Langmuir isotherm

pH	Particle size (μm)	Type of carbon	K_L (dm^3/g)	A_L (dm^3/mg)	q_{max} (mg/g)	R (-)
4	80	C2	2.24	0.51	4.42	0.038
5	80	C2	3.87	0.094	41.20	0.175
6	80	C2	2.67	0.12	23.16	0.147
4–6 ^a	45	C3	29.31	1.59	18.35	0.012
4–6	125	C3	8.33	0.46	17.92	0.041
4–6	250	C3	6.11	0.35	17.68	0.055
4–6	500	C3	8.42	0.52	16.12	0.037
4–6	80	C1	16.09	0.57	28.44	0.034
4–6	80	C2	9.13	0.44	20.81	0.044
4–6	80	C3	5.87	0.38	15.33	0.049

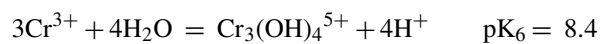
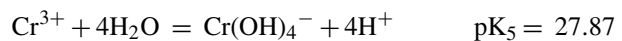
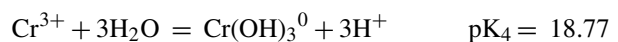
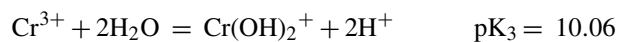
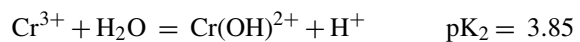
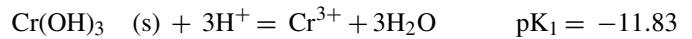
^a Without pH control.

Values of R for chromium activated carbon system have been calculated and are given in Table 3. The R -values calculated indicate that the chromium activated carbon system at different pH, particle size and different types of carbon is favorable adsorption ($R \ll 1$).

3.2.1. Effect of pH on the adsorption isotherm

The effect of pH on the adsorption of Cr(III) onto activated carbon C2 was studied by evaluating the adsorption isotherm at pH values of 2, 4, 5 and 6 as shown in Fig. 1. It was found that activated carbon effective for the adsorption of Cr(III) above pH 2 and below pH 6.5, since Cr(III) at strongly acidic media did not adsorb to the activated carbon matrix. Fig. 1 illustrates that maximum adsorption capacity at pH 5, which approximately twice that for pH 6 and 10 times greater than that for pH 4, as determined by the q_m values as shown in Table 3 and adsorption isotherm in Fig. 1.

Chromium(III) in aqueous solution forms the following complexes [36,37].



To illustrate the distribution of the chromium species at different pH values in aqueous solution, the speciation diagram, shown in Fig. 2 was generated by a computer program based on the above values for equilibrium constants. The term speciation may refer to the description of the abundance of species of an element, and to the reactivity and transformation of a given species into another [38]. According to the speciation diagram, the predominant species below pH 2 is Cr^{3+} and between pH 6.5 and 10 the predominant species is $\text{Cr}(\text{OH})_3$. Since no adsorption of Cr(III) on activated carbon was detected below pH 2, the Cr^{3+} species does not adsorb. At pH 4, the Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$ species

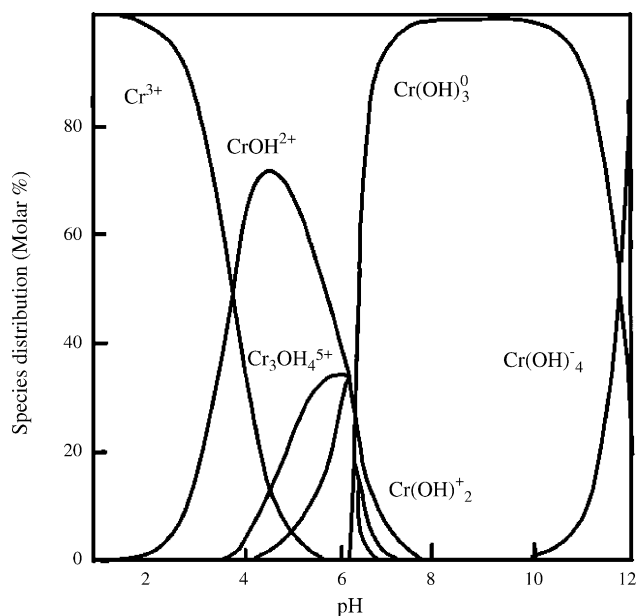


Fig. 2. Speciation diagram for Cr(III) complexes present in aqueous solution.

are present in an approximate distribution of 40 and 60%, respectively. At pH 5, the Cr(OH)^{2+} species dominates accounting for nearly 70% of the chromium present with the other major form as $\text{Cr}_3(\text{OH})_4^{5+}$ accounting for around 20%. At pH 6 the complexes Cr(OH)^{2+} , Cr(OH)_2^+ and $\text{Cr}_3(\text{OH})_4^{5+}$ represent approximately 40, 35, 25% of the aqueous chromium, respectively.

The distribution of species clearly indicates that between pH values of 2 and 4, the complex Cr(OH)^{2+} is selectively adsorbed on activated carbon, but that between pH values of 4 and 6, Cr(III) is adsorbed principally as Cr(OH)^{2+} although the $\text{Cr}_3(\text{OH})_4^{5+}$ complex is also adsorbed. This last conclusion explains the maximum adsorption observed at pH 5, since at this pH, the complexes Cr(OH)^{2+} and $\text{Cr}_3(\text{OH})_4^{5+}$ represent 90 % of the total Cr(III) present in solution.

3.2.2. Effect of particle size on the adsorption isotherm

The effect of particle size on the adsorption of Cr(III) onto activated carbon C3 was investigated by evaluating the adsorption isotherm at size ranges 45, 125, 250 and 500 μm , the experimental results are shown in Fig. 3 and Table 3. It is clear from Fig. 3 that the adsorbent particle size has significant influence on the adsorption process due to change in number of adsorption sites. The removal of Cr(III) as a function of particle size showed that the uptake of metal ion increases with a decrease in particle diameter [39,40], as indicated from values of the Langmuir parameters Table 3. Such an effect is probably due to the small particle size increase the total surface area and therefore the ability of Cr^{3+} to penetrate all the internal pore structure of carbon is very high (viz. reduces the external mass transfer resistance).

3.2.3. Effect of different type of activated carbon on the adsorption isotherm

The effect of activated carbons characteristics on adsorption of Cr(III) was studied by using three types of carbons C1, C2, and C3, which have different characteristics as shown in

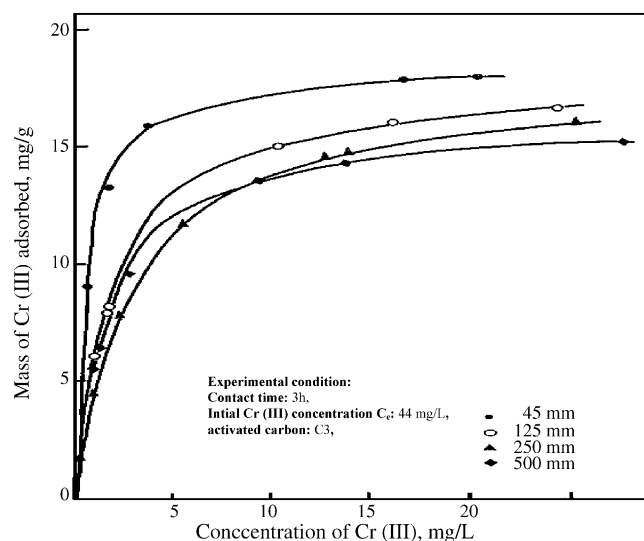


Fig. 3. Adsorption isotherm of Cr(III) onto granular activated carbon (effect of particle size).

Table 2. The experimental data are shown in Fig. 4 and Table 3. According to the parameters in Table 3, the adsorptive capacity increases according to the following order $\text{C1} > \text{C2} > \text{C3}$. Carbon “C1” has the largest surface area (520.66 m^2/g) and appreciable amounts of calcium (333.3 mg/l) and many functional groups, all of these increase the affinity of carbon to adsorb the solute, which could be the reason for giving the greatest difference in adsorptive capacity [41]. The efficiencies of activated carbons

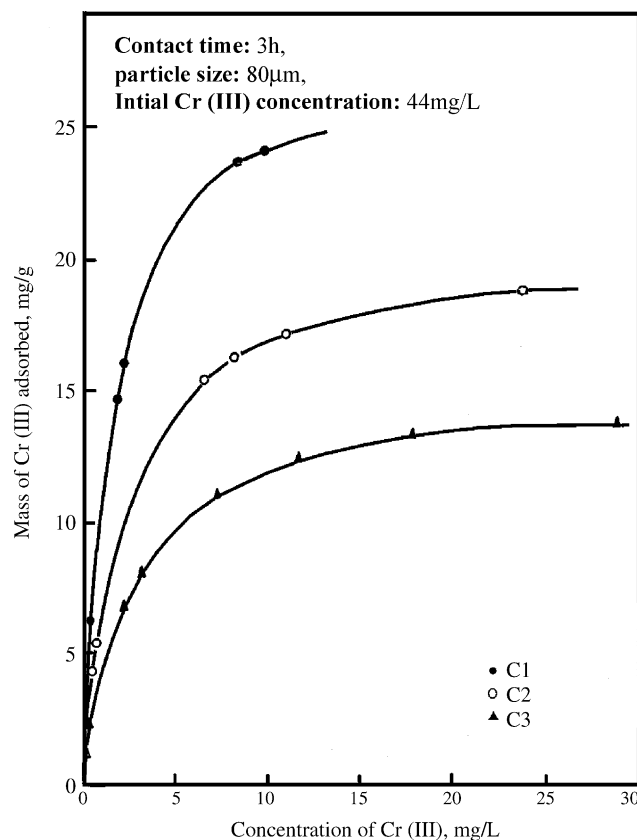


Fig. 4. Adsorption isotherm of Cr(III) onto different types of activated carbon.

for the removal of Cr(III) were found to be 98.86, 98.6 and 93% for C1, C2 and C3, respectively. These results were obtained at conditions of pH (5.5), contact time (3 h), adsorbent dose (5 g/l), initial chromium concentration (44 mg/l) and with particle size (80 μm). It is clear that greater than 99.7% removal of Cr(III) can be achieved when 1 l of 44 mg/l Cr(III) solution is contacted with 5.5 g of activated carbon C1 under experimental conditions of contact time 3h, particle size 80 μm and pH 5.2. Therefore, C1 obtained from sugar factory could be used as efficient and economic adsorbent for removal of Cr(III) from tannery wastewater. Obviously, the adsorptive capacity of activated carbons depends on its physical and chemical characteristics as well as on the raw material from which its produced and activation process.

4. Conclusions

1. The adsorption isotherms data referred to C1 has more adsorption capacity for Cr(III) removal than C2 and C3. C1 obtained from local sugar factory (El-Hawamdia sugar company, Egypt) is effective for removal of chromium.
2. The three adsorbent materials C1, C2 and C3 are efficiently working for the Cr(III) removal between the pH 5.0–6.0, which is more preferable at pH 5.0.
3. The adsorption capacity of Cr(III) onto activated carbon increases by decreasing particle size. The maximum adsorption of Cr(III) at particle size ranges 45 μm .
4. Further suggesting the use of C1 over the use of C2 and C3 for the removal of Cr(III) from tannery wastewater. As C1 being waste products are cheaper and easily available from sugar processing industries, it is expected to be an economical adsorbent material for removal and recovery of Cr(III) from tannery wastewater and purification of tannery effluent.

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