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Efficacy of Watermelon *(Citrullus Lanatus)* Rind Charcoal for Chromium Removal from Tannery Wastewater

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ABSTRACT
Over recent years, sustainable development has been more appreciated to achieve the goal of a safe environment with the proper waste management system. Since the complete reduction of waste generation is inevitable, waste management is the best possible solution for a sound environment. In this proposed approach, watermelon rind charcoal was used as an adsorbent to remove chromium from tannery wastewater. Following batch experiment process the system was optimized by different parameters: charcoal dose, contact time and adsorption kinetics and the physicochemical characteristics of both raw and treated effluents were analysed.The chromium content in raw wastewater and treated wastewaters were 2733.4 mg/L and 5.536 mg/L respectively with 99.8% chromium removal efficiency. Additionally, it removes the chloride content by 56.86%. This method revealed the significant potential of watermelon rind in chromium removal from tannery effluent.

Keywords: Chromium, Tannery effluent, Watermelon Rind.

1. Introduction

Leather making is a traditional industry existing since time immemorial, certainly over 5000 years [1]. The term leather making generally refers to the tanning process where putrescible raw hides/skins are converted to leather. Many processes have been practised throughout history but at present more than 90% of the global leather production of 18 billion sq. ft. are tanned through chrome tanning process [2].It’s faster and more reliable reaction with collagen matrix enhanced the popularity over the previously followed vegetable tanning process [1].

During tanning process,the pickle pelt reacts with60-70% of total chromium saltsand the rest of 30-40% of the chromium remains in the solid and liquid phases (especially as spent tanning liquor) [3].Everyday approximately 1.25 tons of chromium is discharged into the river and around 1.6 tons is discharged from the tannery effluent where peak discharge is considered as 21000 m^3/day[4].

In general, chromium is found in itstrivalent chromium Cr (III) andhexavalent chromium Cr (VI) form[5]. The Cr (VI) is extremely toxic and may cause contact allergic dermatitis on the skin and may also be a trigger for manydiseases [6]. Thus, in spite of its popularity chrome tanning causes great concern to humanity.

Numerous treatment methods [7]such as ion exchange [8], reduction [9], chemical precipitation [10], membrane separations [11], electrochemical precipitation [12], photocatalytic reduction [13], have been developed for chromium remediation. Most of theseprocesses are successful for purging chromium from wastewater but the highly expensive system and the toxic materials produced after treatment reduce its popularity.

An adaptable worldwide method for removing organic and inorganic pollutants from wastewater is adsorption using activated carbon as adsorbent[14]. Adsorption technique is verified as low cost, easy tomaintain and more economical if the raw material of the adsorbent is available[15].The precursors to be a good adsorbent is a large surface area, low volume pores, good physicochemical properties, resistance against the atmospheric change and do not produce perilous substance while conducting adsorption [16].

In the recent years, many low cost, non-conventional adsorbents include rice polish [17], sawdust [18],agricultural byproduct [19], natural zeolite [20],clay [21], polyaniline coated on sawdust [22], eggshell and powered marble [23],*Caricapapaya* plant [24]and so on are developed.However, not all of these adsorbents have completely been investigated. Thus, an attempt has been taken in the research to make the processcost-effective, environment-friendly, and industrially feasible to draw out chromium from the wastewater [7].

Watermelon is a very common fruit grown in the tropical and subtropical areas. In 2016, global production of watermelons was 117 million tons with China alone accounting for 68% of the total [25].Bangladesh produced about 284845 metric tons watermelon in the fiscal year of 2011-2012 [26].In a watermelon, the flesh part, rind and seed constitute approximately 68%, 30% and 2% respectively [27].Watermelon rind is disposed of as waste, which causes an environmental pollution. Proper management is one of the ways to make the environment clean.

In this study, watermelon rind was used to produce charcoal adsorbent to remove chromium from the wastewater.The investigationcould fulfil the purpose of chromium removal from tannery wastewater using a low-cost adsorbent prepared from watermelon rind which is generally discarded as waste.

2. Experimental

2.1 Sample collection

Chrome containing wastewater was collected from the SAF Leather Limited, Khulna, Bangladesh.The chrome liquor was collected in a high-densitypolyethylene container.Before collecting the chrome liquor the container was washed with diluted nitric acid according

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to the standardized laboratory method. The industrial wastewater was primarily filtered to remove unexpected suspended solids and the filtered liquor was used for treatment. Raw watermelon rinds were collected from the dustbin and domestic waste.

2.2 Charcoal preparation

The collected watermelon rinds were sun-dried.Afterwards, it was burnt and crushed with mortar to produce a powder. Lastly, the required size of the charcoaladsorbent was obtained by sieving on 80-mesh.Fig. 1(a) and Fig. 1(b) show the raw watermelon rind and prepared charcoal respectively.

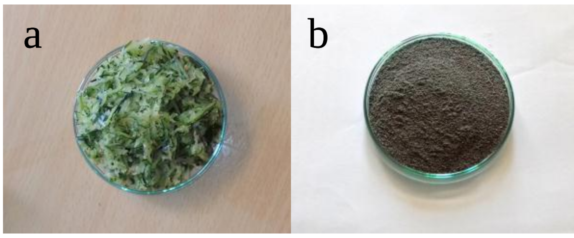

Fig.1 Raw watermelon rind**a)** and prepared charcoal **b)**

2.3 Reagents

The reagents that were used in the experiment were pure concentrated nitric acid (Merck Specialties Private Limited, Worli, Mumbai), sulfuric acid (Merck Specialties Private Limited, Worli, Mumbai), perchloric acid (Merck, India), ammonium iron (Merck, India) sulfate hexahydrate (Merck Specialties Private Limited, Worli, Mumbai) and *N*-phenyl anthranilic acid (Loba Chemie, India), filter paper (Whatman No. 1), anti-bumping agent glass beads (Loba Chemie, India). All of the reagents were collected from local scientific store, Khulna, Bangladesh.

2.4 Characterization of Wastewater

Chromium content, electrical conductivity (EC), salinity, chloride (Cl^-) content, total dissolved solids (TDS), pH were measured in the experiment.

2.4.1 Chromium determination

Quantitative analysis of chromium in the waste liquor and treated liquor was ascertained by the titrimetric method according to the Society of Leather Technologist and Chemists (1996) official method of analysis SLC 208 (SLT6/4) [28].AT first, a 500 mL conical flask was filled with 25 mL sample and 20 mL nitric acid and 20 mL of perchloric acid and the sulfuric acid mixture was added into it. Then heat was applied gently to boil the mixture until it became a pure orange-red colour and the boiling was continued for one minute after the point had been reached. Later, the flask was taken aside from the heating source before exhilaration. Afterwards, the flask was inserted into a cold bath for rapid cooling and then 100 mL distilled water was carefully poured into the flask with glass beads. The heat was applied for 10 minutes to make the mixture chlorine free and after that 10 mL of 30% (v/v) sulphuric acid was carefully added. Finally,when the mixture was cooled, titration was performed with freshly prepared 0.1N ammonium iron (II) sulphate solution with six drops of N-phenyl anthranilic acid as an indicator and the end colour was pointed out as a colour change from violet to green.

2.4.2 Determination of pH

pH of the raw chrome tanning wastewater and treated liquor was measured using calibrated pH meter (UPH-314, UNILAB, USA).

2.4.3 Determination of TDS, EC and salinity

After calibrating the conductivity meter (CT-676, BOECO, Germany) with standard solution TDS, EC and salinity were measured.

2.4.4 Chloride (Cl^-) determination

Chloride content in the chrome tanning wastewater and after treatment was measured by APHA standard argentometric method [29]. A 100 mL sample was taken in a conical flask and pH was adjusted in the range of 7 to 10. Then, 1.0 mL potassium dichromate indicator was added. After that, the solution was titrated with silver nitrate as titrant (0.0141N) to a pinkish yellow endpoint. The titrant was standardized by the sodium chloride (0.0141N) solution.

2.5 Characterization of charcoal

The charcoal (pure and chromium loaded) samples were analyzed using Fourier transform infrared spectrometer (FTIR, Spectrum 100, PerkinElmer, USA) with an attenuated total reflectance (ATR) accessory.Infrared spectra were recorded at a resolution of 4 cm^{-1} and 20 spectra were averaged to reduce the noise.

2.6 Treatment of chromium-containing wastewater

Batch-wise chromium removal test was conducted with the prepared charcoal. The scheme for the treatment of chrome tanning wastewater is shown in Fig. 2.

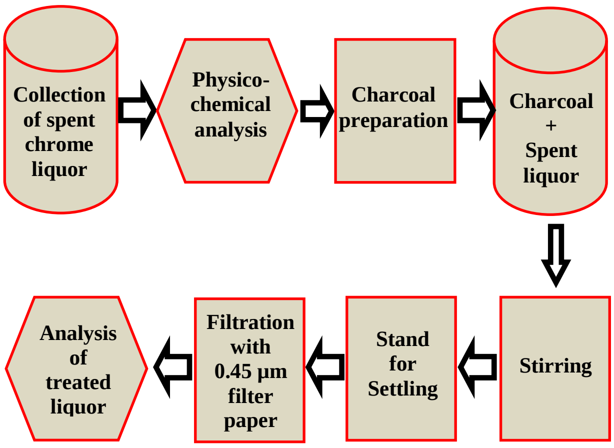

Fig.2 Flow diagram of the treatment process

At first, the chemical and physical characteristics of raw wastewater was examined and then percolated through

0.45 µm pore size filter. Then, 40 mL of the filtrate was mixed with the proposed charcoal.The charcoal mixed wastewater was stirred over a fixed period of time. After settling, the mixture was then filtrated through 0.45 µmpore size filter and again chromium content measurement was done.

2.7 Process optimization

Optimization of the whole process was carried out for maximum chromium removal efficiency [24].Tests were carried out to optimize the chromium removal parameters: adsorbent dose, contact time and relative pH. The optimized conditions were established by investigating the removal efficiency of chromium.

2.8 Investigation of a kinetics model

To investigate adsorption kinetics 33 g of charcoal was taken in 833 mL (as per optimum dose 2 g/40 mL of wastewater) spent chrome liquor. At constant stirring 40 mL treated liquor was taken carefully as possible after 1, 3, 6, 9, 15, 21, 27 and 35 minutes. Then the liquor was filtered and the chromium content of the filtrate was measured.

In an adsorption process, it is supposed that the rate isproportional to the difference between the amounts of adsorption attime t and the adsorption capacity of adsorbent (a-x) [30]. Then the simple linear form of Lagergren's pseudo-first order reaction can be summarized as,

$$\ln(a - x) = \ln a - K_1 t$$

$$\text{or, } \ln\frac{(a - x)}{a} = -K_1 t \ldots\text{(i)}$$ [24]

The pseudo-first order reaction of Lagergren's first order reaction is described in Eq.(i), where x and a are denoted as the amounts of adsorption at time t and at equilibrium (mg/g) respectively and k_1 as the first-order rate constant (min^{-1}).

The value of K_1 and correlation coefficient (R) can be obtained from the linear plot of ln(a-x)/a versus time (t).

Kinetic analysis for the pseudo-second-order reaction can be formulated from Eq. (ii):

$$x = \frac{a^2 K_2 t}{1 + K_2 a t}$$

$$\text{or, } \frac{x}{a(a - x)} = K_2 t \ldots\text{(ii)}$$ [24]

Wherex and a are the adsorption capacity (mg/g) at time tand at equilibrium respectively, and $K_2$is theequilibriumrate constant for adsorption process (g/mg.min).

The value of K_2 can be calculated from the slope and the intercept of the plots of x/a(a-x) versus time (t). This model supports two reactions occurring at the same time:the first one is fast and reaches equilibrium quickly and the second one is slow and can continue for a long time.

3. Result and discussion

3.1 Characteristic of charcoal

Fig. 3 depicts the FT-IR spectrum of charcoal before and after the adsorption of chromium. The figure reveals changes in the peak intensity.

Fig. 3(a) shows a broad region around 3468 cm^{-1}indications the presence of hydroxyl group, N-H group and C=O group around 1867 cm^{-1} wavelength. The -OH, -NH, carbonyl and carboxylic groups have been reported as significant sites for metal ions adsorption [31]

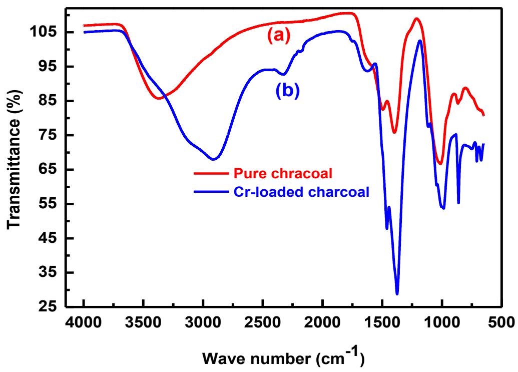

Fig.3FT-IR spectrum of pure charcoal (**a**) and chromium-loaded adsorbent (**b**)

However, in the case of Fig. 3(b) there is a noticeable shift in the peak. Here, C-H, C=H groups are found at around 3000 cm^{-1} with additional C-H and C-O functional groups at 1385 cm^{-1} and 1220 cm^{-1} wavelength respectively. This ensures the involvement of the hydroxyl and other groupsof pure charcoal in the adsorption process.

3.2 Effect of charcoal dose

The charcoal dose was observed by the batch optimization process. Five samples of 40 mL chrome liquor were treated with 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g of charcoal.

After 10 minutes of stirring and 10 minutes of settling, each sample was filtered and the amount of chromium was measured.

Fig. 4 shows the change in removal efficiency and pH with the change in charcoal dose. It is clear that the increase of charcoal dose results in the increase in the efficiency and pH. This may be because the more amount of charcoal is added; the more chromium can be adsorbed to the surface, thus removing more chromium. At 2.0 g dose per 40 mL of spent liquor, the removal efficiency is 99.5% at a pH 8.5. At this point, the efficiency reaches at a saturation point. Thus, 2.0 g per 40 mL of liquor is considered as an optimum dose.

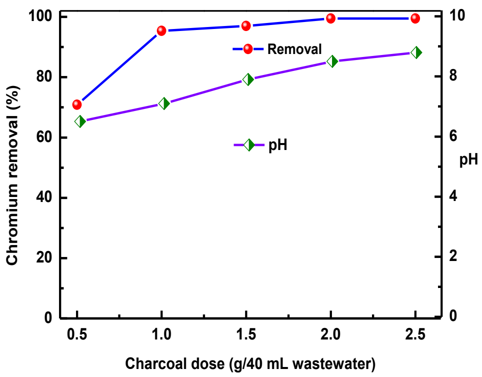

Fig.4 Batch wise treatment process at different charcoal doses: 0.5, 1.0, 1.5, 2.0, and 2.5 g; in each batch 40 mL wastewater with fixed 10 min contact time was used

3.3 Effect of contact time

The adsorption efficiency depends on the availability of the adsorbent surface as well as the time allowed for the interaction of adsorbent with the adsorbate. Fig. 5 depicts the change in removal efficiency due to the change in contact time. Here batch optimization process was followed using 6 samples with optimum dose i. e. 2.0 g per 40 mL of waste liquor where the contact time was 1, 3, 6, 9, 12 and 15 minutes respectively.

The increase in contact time allows the adsorption to take place for a longer time, thus increasing removal efficiency.

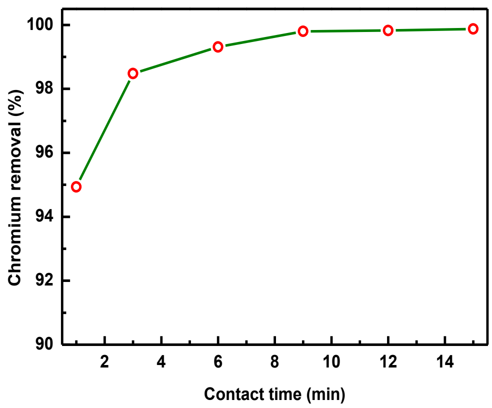

Fig.5 Batch wise chromium removal efficiency on different contact time: 1, 3, 6, 9, 12 and 15 min; in each batch 40 mL wastewater with fixed 2 g charcoal was used

At 9 minutes, the removal efficiency is 99.8% and after that the change is negligible. So, in this experiment, the optimum contact time was considered 9 minutes.

3.4 Kinetics Model

Adsorption kinetics refers to the rate of adsorption at a constant pressure or concentration and is employed to measure the diffusion of adsorbate in the pores of the adsorbentand the percentage of the incident adsorbate molecules.

Kinetic models are used to test experimental data to verify the mechanism of adsorption and potential rate controlling steps like mass transport and chemical reaction processes [32].

Fig. 6 and Fig. 7 describe the graph for adsorption kinetics of pseudo-first and pseudo-second-order reaction respectively. The value R_1^2= 0.78598 and R_2^2= 0.9069 for pseudo-first-order and pseudo-second-order kinetics are depicted from the graphs respectively.

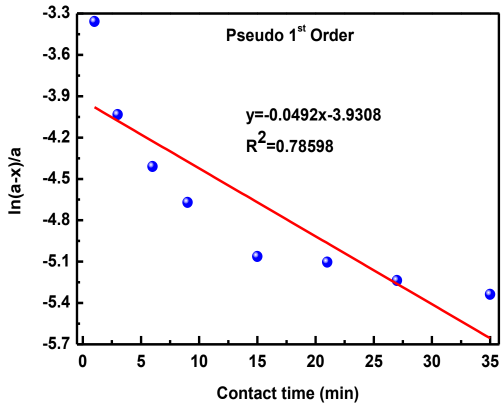

Fig.6 Adsorption kinetics of pseudo-first order

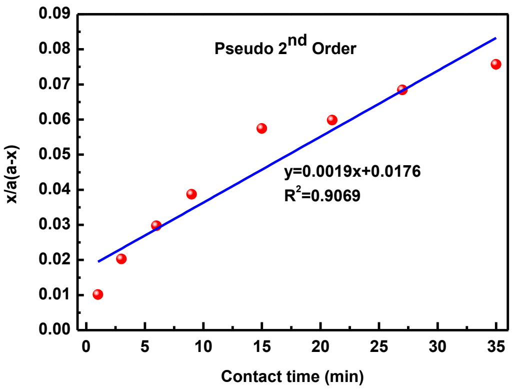

Fig.7 Adsorption kinetics of pseudo-second order

It could be clearly decided that the pseudo-second-order kinetics provided a better description for the adsorption of the Cr (III) onto adsorbent than a pseudo-first-order kinetics equation.

3.5 Treatment process efficiency

The results of the treatment process with optimum conditions are depicted in Table 1. The physicochemical parameters of wastewater obtained after treatments are chromium 5.536 mg/L, pH 8.3, TDS 36.6 mg/L, EC 84.9 mS, salinity 54.4 ppt and chloride (Cl^-) 7700 mg/L.

It shows that after treatment chloride (Cl^-) was high from the discharge limit but it was reduced at a noticeable level.This may be because chloride has a tendency to co-precipitate with other ions.

Table 1 Data comparison with Bangladesh standard (ECR 1997)

Parameters	Raw sample	Treated sample	ECR[33]
Cr (mg/L)	2733.4±3.75	5.536±2.3	2.0
pH	4.2±0.2	8.3±0.5	6–9
TDS (g/L)	28.28±0.2	36.6±0.5	2.1
EC (mS)	58.2±0.2	84.9±0.4	1.20
Salinity (ppt)	38.76±0.7	54.40±0.09	-
Cl^-(mg/L)	17850±11.3	7700±9.6	600

The removal efficiency of chromium at optimized condition was 99.8% and the reduction of chloride was 56.86%. During this treatment, the prepared charcoal acts as adsorbent and the inorganic and organic pollutants are adsorbed by the charcoal surface. Thus, after filtration, the pollutants are removed with the adsorbent from the wastewater and reduce Cr, chloride and salinity.

4. Conclusion

This investigation is a potential approach to remove chromium from tannery wastewater as well asa new applicationof watermelon rind as an adsorbent in tannery industry. Considering the huge production of watermelon every year, its rind could be marked as available, low-cost raw material. The treatment process implies that the charcoal is prepared from a waste material and no additional chemicals are required.In this batch-wise technique, the removal efficiency of chromium at 2 g per 40 mL of wastewater was 99.8% after 9 minutes of stirring and additionally, it also removes the chloride content by 56.86%. Several methods might have been tried before but considering the potential of this method, it could be easily adopted industrially as a column test process with some further research on cost analysis and input-output ratio.

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