

ABSORPTIVE REMEDIATION OF CHROMIUM CONTAMINATED TANNERY EFFLUENTS BY UTILIZATION OF MAHAGONI TREE (*SWIETENIA MAHAGONI*) BARK

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Abstract- The presence of chromium (III) in the wastewater is one of the major concerns for the tannery industry in Bangladesh. In this study the removal of chromium (III) from tannery effluent has been carried out by adsorption method using abundantly available *Swietenia mahagoni* bark which is available all over Bangladesh. Various factors influencing the uptake of chromium, viz. and quantity of bark, concentration of chromium (III) and duration of treatment have been optimized. The study was performed using batch experiments with chemical industry effluent having Cr (VI) in higher concentration. Parameters such mass of adsorbate, concentration of adsorbent and time of contact were optimized. It was observed that, under optimum conditions, the percentage efficiency of removal of Cr (VI) was up to 99.7%. The results indicated that the *Swietenia mahagoni* bark has good removal efficiency. About 82% and 99.4% Cr removal was achieved by using 0.5 gm. and 1.5 gm. adsorbent for wastewater initial concentration of 3261.76. Significant change on BOD, COD and Turbidity were also found after treatment. So the use of *Swietenia mahagoni* bark as bio-sorbent to remove chromium from Cr tanned waste water could be considered as very successful, and it can be an effective solution to the problem created by chrome tanned waste water to the environment or to the sustainable waste management.

Keywords: Tannery effluents, Chromium (III), *swietenia mahagoni*, COD, BOD, FTIR

1. INTRODUCTION

Worldwide, the liberate of different hazardous pollutants to the environment is severely pollute the water-born ecosystem [1]. These organic and inorganic compounds with both pollutants simultaneously exist in the effluent and environment [2], [3]. Especially, leather making refers to the tanning process where putrescible raw hides/skins are transformed to leather. Throughout the time, many methods have been studied but contemporary more than 90% of the world leather productions of 18 billion sq. ft. are tanned through chrome tanning process [4]. It's prompt and more feasible reaction with collagen matrix increased the popularity over the prior followed vegetable tanning process [5]. In tanning process, the pickle pelt reacts only 60-70% of total used chromium salts and the rest of 30-40% of the chromium residue in the solid and liquid stage (especially as spent tanning liquor) (A. Ismailia et al., 2005). Now-a-days approximately 1.25 tons of chromium is released into the river and around 1.6 tons is pouring out from the tannery wastewater where peak emission is considered as 21000 m³/day [6]. Commonly, Chromium waste exists in concentration of Cr (VI) and Cr (III) in the soils which seems the greatest contaminating concern globally. The heavy metal can exist in oxidation states ranging from -2 to +6, but trivalent chromium (Cr³⁺) and hexavalent chromium

(Cr⁶⁺) are the most commonly observed due to their stability in the pH and redox range of the environment [7]. Tannery effluents are unlikely to contain chromium and its dichromate's form is toxic to fish life since they swiftly penetrate cell walls [8]. Besides that, the desired use to chromium creates high anxiety among the humankind. Different treatment techniques have been used for the elimination of metal from wastewater; this includes techniques such as membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis, adsorption, and photoreduction. Most of these procedure are fruitful for purify chromium from wastewater but the system is overpriced and the poisonous materials induced after treatment lessen its in demand. The congenial method for reducing organic and inorganic pollutant from effluents is adsorption, utilizing activated carbon as an adsorbent [9]. Recent time, many cost-effective, original adsorbents involve like, rice polish, sawdust, agricultural byproduct, natural zeolite, clay, polyaniline coated on sawdust, eggshell and powered marble, *Caricapapaya* plant and so on . *Swietenia marcrophylla* commonly known as mahogany in Bangladesh is a large deciduous tree with an umbrella-shaped crown [10]. Now it became naturalized in some introduced ranges including roads and highways and at homestead areas. The bark of the tree are commonly reduced while wood processing and afterthat

it is settled in soil. Now, recycle of organic and inorganic waste is a major concern now-a-days all over the world [11].

In this study, *swietenia mahagoni* bark was used to prepare activated carbon charcoal which reduces chromium from the wastewater as an adsorbent. The *swietenia mahagoni* tree is available and its acts as eco-friendly adsorbent to discriminate hazardous metals present in tannery effluents. The utility of chromium removal was investigated by inspecting different parameters, e.g. adsorbent dose, contact time, p^H .

2. MATERIALS AND METHODS

2.1 Sample Collection

Chromium containing tannery effluent was collected from the SAF Leather Limited, Jessore-Khulna Hwy, Noapara Paurasava, Bangladesh. The wastewater-containing chromium sample was collected in a high density polyethylene polymer container, early clean with diluted nitric acid and send to the laboratory without delay for the experiment. The *swietenia mahagoni* bark was collected from Star Saw Mill & Timber, 61/1, Rupsha Strand Road, Khulna, Bangladesh. After collecting bark, it was organized in the laboratory for conducting experiment.

2.2 Adsorbent Preparation

The collected *swietenia mahagoni* bark was cut into small pieces then sun-dried under open sunlight for several days until its weight remains constant. Afterthat, it was burnt at 450-550 °C in aerobic condition, cooled and grinded with mortar to produce powdered like charcoal. Finally, obtaining desired size charcoal, the adsorbent was sieved with 60 mesh and restore in a plastic bottle for the experiment.

2.3 Reagents

The reagents that were used in the experiment, concentrated nitric acid (Prasol Chemical Pvt. Ltd., Mumbai) perchloric acid (MerckKGaA, Germany), sulphuric acid (Merck KGaA, Germany), Ammonium ferrous sulphate (Merck, India), N-phynylanthranilic (Loba chemie, India), glass bed (Loba Chemie, India) and filter paper (Whatman No. 1) were purchased from local scientific store(City Scientific), Khulna, Bangladesh.

2.4 Characterization of tannery wastewater

2.4.1 Determination of Chromium content

Chromium content in the untreated spent liquor and after treatment in the filtrate was measured by the titrimetric method by following the official methods of analysis Society of Leather Technologist and Chemists (1996) 208 (SLT6/4)[12]. A 25 mL sample was taken in 500 mL conical flask. 20 mL concentrated nitric acid was added followed by 20 mL perchloric acid and sulphuric acid mixture; the flask was gently heated until the mixture had become a pure orange-red color and after reaching the color boiling was continued for one minute. The flask was removed from the heating source and as soon as ebullition had ceased the flask was rapidly cooled by swirling in cold water bath. Carefully, 100 mL distilled water was added with a few glass beads and then again boiled for 10 minutes to remove free chlorine. Then, 10 mL 30% (v/v) sulphuric acid was added and the mixture

was cooled to room temperature. The mixture was titrated with freshly prepared 0.1N ferrous ammonium sulfate solution with five to six drops of N-phenyl anthranilic acid as an indicator. The end color was indicated by a color change from the violet to green.

2.4.2 Determination of p^H

The p^H of the spent chrome liquor was measured by using the p^H (UPH-314, UNILAB, USA) meter. Before measuring, the meter was calibrated with the standard buffer solutions.

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 Determination of BOD₅

Biochemical oxygen demand of the spent chrome liquor and treated liquor were determined by IS: 3025 (Part 44) – Reaffirmed 2012, (APHA-5210 B) method. Dilution water was ready to put required volume or water in a bottle and include phosphate bufer, magnesium sulfate, calcium chloride, and ferric chloride solutions. Prior testing, p^H of the sample was measured. Unless p^H is within the acceptable range (6.5–7.5), pH was calibrated with sulfuric acid or sodium hydroxide solution. Desired sample volume was added to 300 mL BOD bottle. Bottle was filled with enough dilution water so that array of stopper will displace all air, leaving no bubbles. The diluted water (blank) was also incubated as a rough check on quality of diluted water and neatness of incubation bottles. Initial DO was measured with DO meter (DO-580, BOECO, Germany). BOD bottle was incubated at 20±1 °C. After 5 days incubation, DO was determined and calculated as BOD₅.

$BOD_5 = \{Initial\ D.O - final\ D.O\ (after\ 5days)\} \times Dilution\ Factor$

2.4.5 Determination of COD

COD was determined following the APHA standard method (IS: 3025 (Part-58)-Reaffirmed 2012, APHA-5220 C). Diluted tannery effluents sample was position in culture tube (pewashed with 20% sulfuric acid) and potassium dichromate digested solution was added. Sulfuric acid was carefully run inside of the tube so that an acid layer is formed under sample-digestion solution layer. Tube was tightly capped and inverted several times to mix properly. Tube was placed in block digester preheated to 150°C and refluxed for 2 h behind a protective shield. Tube was cooled to room temperature and placed in test tube rack. Culture tube cap was removed and added small TFE-covered magnetic stirring bar. 0.05 to 0.10 mL (1–2 drops) ferroin indicator was added and stirred rapidly on magnetic stirrer while titrating with standardized 0.10 M ferrous ammonium sulfate. The end point was a sharp color change from blue–green to reddish brown, although the blue–green was re-exists within minutes. Similarly, a blank containing the reagents and a volume of distilled water equal to that of the sample was refluxed and titrated.

$$COD\ (mg/L) = \frac{(blank\ value - sample\ value) \times 8 \times 0.1 \times 1000}{Volume\ of\ Sample}$$

2.5 Characterization of Charcoal

The adsorbents(pure and chromium loaded) was analyzed using Fourier Transform Infrared Spectroscopy

(FTIR, Spectrum 100, PerkinElmer, USA) with an exhausted 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

The chromium removal test was carried out group-wise by utilizing prepared charcoal. The following Fig.01 reveals detail of the wastewater treatment process.

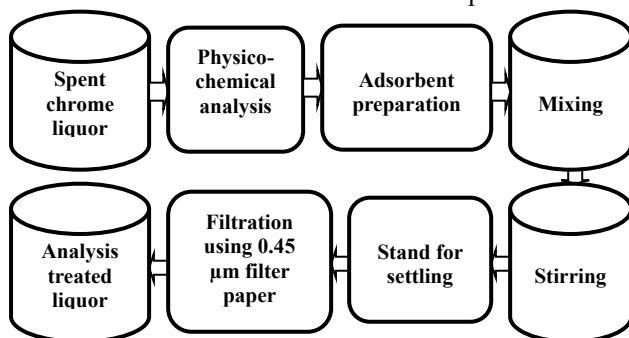


Fig.1: Schematic flowchart for the chromium removal treatment process.

Primarily, the physicochemical parameters of the untreated chrome tanning wastewater were analyzed and filtrate through 0.45 µm pore size filter. After that, 75 mL filtrate wastewater was mixed with the prepared adsorbent and mixture was stirred over a fixed period of time. Afterthat, settling for a fixed period, then the mixture was filtered through 0.45µm pore size filter. Later, the chromium content was measured by using the same procedure as mentioned in 2.4.1.

2.7 Process Optimization

The method was optimized for acquiring maximum removal efficiency. In group-wise examination, various parameters: charcoal dose, contact time and relative pH were optimized. The optimized conditions were established by investigating the chromium removal efficiency.

2.8 The study of kinetic model

Normally, we can know the rate of adsorption by analyzing adsorption kinetics. To examine the kinetics models of chromium ions adsorption onto *swietenia mahagoni* bark adsorbent, pseudo-first-order and pseudo-second-order kinetic models were tested. The linear form of the pseudo-first-order kinetic model can be written in Eq. (1).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \dots \dots \dots (1)$$

$$\Rightarrow \ln \frac{Q_e - Q_t}{Q_e} = -K_1 t \dots \dots \dots (2)$$

In equation (2), where, Q_e (mg/g) is the amount of chromium adsorbed per unit mass of the adsorbent at equilibrium; Q_t (mg/g) is the amount of chromium adsorbed per unit mass of the adsorbent at time t (min); K_1 (per min) is the equilibrium rate constant of the pseudo-first-order model.

The pseudo-second-order kinetic was analyzed based on Eq.(3):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e} + \frac{t}{Q_e} \dots \dots \dots (3)$$

$$\Rightarrow \frac{Q_t}{(Q_e - Q_t)} = K_2 t \dots \dots \dots (4)$$

In equation (4), where, K_2 (g/mg/min) is the rate constant of the pseudo second-order equation.

2.9 The study of Adsorption Isotherm

Interaction between adsorbent and adsorbate were described in adsorption isotherm. To know the adsorbent capacity and optimizing adsorbent consumption, isotherm was the essential indicator. Here, Langmuir and Freundlich isotherm were studied to interpret the adsorbent characteristics of adsorption process. Langmuir model express the uniform energy adsorption onto the solid surface including, a single-layer adsorption in the homogenous sites and the homogenous structure of adsorbent [13]. The linearized Langmuir equation is represented by Eq. (5):

$$\frac{1}{Q_e} = \frac{1}{C_e} \times \frac{1}{Q_m K_L} + \frac{1}{Q_m} \dots \dots \dots (5)$$

In equation (5) where, Q_e (mg/g) is the amount of chromium adsorbed at equilibrium C_e (mg/L) is the equilibrium concentration chromium in solution Q_m is (mg/g) the maximum chromium adsorption capacity; K_L (L/g) is the Langmuir constant related to the energy of adsorption.

In case of Freundlich isotherm, data were analyzed in the following way: The Freundlich isotherm equation is expressed in Eq. (6).

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \dots \dots \dots (6)$$

In equation (6), where k_f is a Freundlich constant which shows the adsorption capacity of adsorbent and n is a constant which shows the greatness of relationship between the adsorbate and adsorbent.

3. RESULTS AND DISCUSSION

3.1 Characteristics of charcoal

The FT-IR spectrum of the charcoal before and after the adsorption of chromium is shown in Fig.2. The figure shows a shift in the peak intensity. The FT-IR was determined to understand the changes of frequency in the functional groups of the charcoal due to adsorption of chromium. This indicates that various functional groups, which were responsible for the removal of chromium by the charcoal. The salient features are: strong and broadband centered at 2358.94cm⁻¹ characteristic of triple bonds e.g. C≡C, C≡N stretches arising from the surface triple bond groups. Weak and broad band centred at 1404cm⁻¹ assignable to the aliphatic C=C group. The band at 873.75cm⁻¹ arising from =C-H group. The peak at 1085cm⁻¹ may correspond to stretching frequency of carbonyl(C=O) group. The multiple number of peaks around 500 cm⁻¹ (524, 509 & 503 cm⁻¹) may correspond to C-Cl, C-Br group of *swietenia mahagoni* bark.

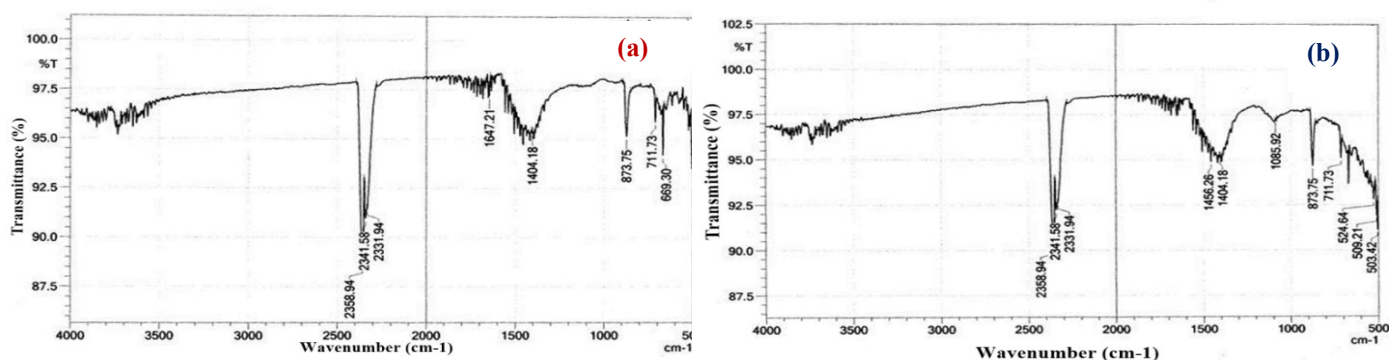


Fig.2: FT-IR spectrum of: (a) fresh *swietenia mahagoni* bark charcoal and (b) chromium loaded charcoal

3.2 Characteristics of the spent chrome liquor

Results indicate that wastewater had strong pollution loads because it contained higher quantities of pollutants e. g. high chromium content, BOD, COD,

strongly acidic ($4.0 > \text{pH}$). Wastewater containing chromium is threatening to the environment, it is very important to treat the chrome wastewater properly to reduce its polluting potency.

Table 1: Data comparison with Bangladesh standard (ESR 1997) [14]

Parameters	Raw sample	Treated sample	Discharge standard to Public Sewerage System
Cr (mg/L)	3261.76	18.684	2.0
pH	3.9	6.9	6–9
BOD (mg/L)	3154	121	250
COD (mg/L)	4199	289	400
EC (mS)	69.2	84.1	1.20
Salinity(ppt)	36.66	49.57	-

3.3 Charcoal dose optimization

The dose of adsorbent is the most important parameter that has a significant effect on the chromium removal. Chromium removal efficiency on an adsorbent dose is depicted in figure (Fig.3). It is clear from the figure that chromium removal efficiency was increased with the increasing of adsorbent dose. For 0.5 g, 1 g, 1.5 g, 2 g, 2.5 g, 3g and 3.5g of adsorbent doses the relative percentage of chromium removal efficiency was 82.051%, 92.829%, 99.427%, 99.575%, 99.702%, 99.702%, and 99.702% respectively. At adsorbent dose 3g for 30 mL, chromium removal efficiency was 99.702% and after that no significant change occurred. Therefore, it was anticipated that the maximum removal of chromium occurred with 3g adsorbent dose for every 30 mL wastewater where pH was 6.9.

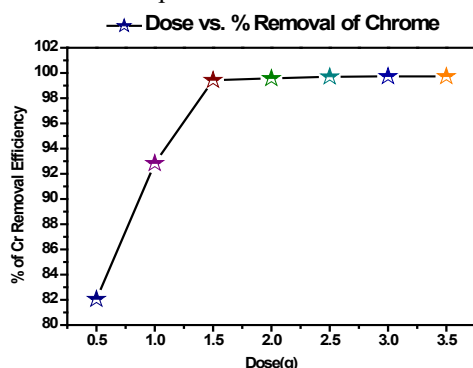


Fig.3: Chromium removal efficiency vs. dose

3.4 Contact time optimization

Contact time is one of the most important parameter for the removal of chromium in the spent chrome liquor. In figure (Fig.4) shows the chromium efficiency on contact

time. From the figure (Fig.4) shows that chromium removal efficiency was gradually increased with increasing the contact time. The chromium removal efficiency with a fixed dose of 3g/30 mL for different contact times- 5 min, 10 min, 15 min, 20 min, 25 min and 30 min was 97.878%, 99.045%, 99.491%, 99.512%, 99.533% and 99.533% respectively and after that removal efficiency was unchanged. Thus, it was assumed that extreme removal of chromium happened at 15 min contact time. For the first two batches, the adsorption rate increases more rapidly. After that, the reaction becomes lower when the remaining active sites are less available and the equilibrium phase reached.

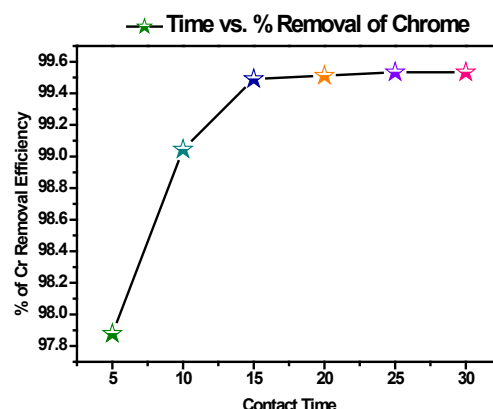


Fig.4: Chromium removal efficiency vs. contact time

3.5 Adsorption kinetics

From the figure (Fig.5), the value of R_1^2 (0.9604) and R_2^2 (0.9723) is obtained for pseudo-first-order and

pseudo-second-order kinetics respectively. It could be clearly sentenced that the pseudo-first-order kinetics did not provide a good description for the adsorption of the Cr (III) onto adsorbent rather pseudo-second-order kinetics equation can, as a plot of $x/a(a-x)$ against time, t provided a good fit ($R^2 = 0.9723$). Data of first order and second order kinetics, according to this model, two reactions occur, the first one is fast and reaches equilibrium quickly, and the second slows that can continue for a long time [11].

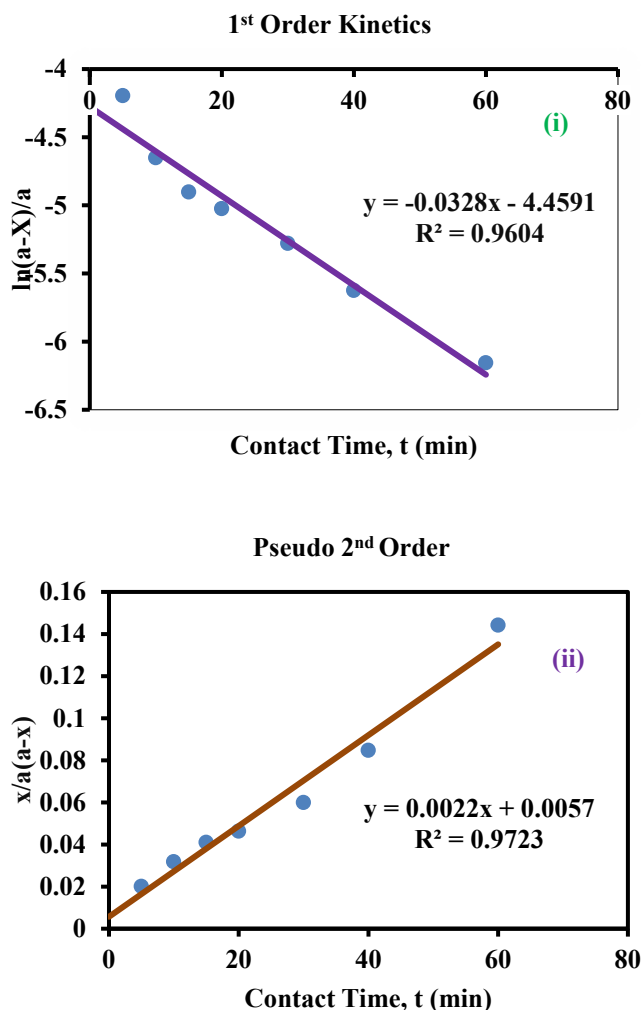


Fig.5: Adsorption kinetics: (i) Pseudo-1st order kinetics and (ii) Pseudo-2nd order kinetics.

3.6 Adsorption isotherm

According to figure (Fig.6), the results indicate that the Langmuir model is well fitted with the adsorption data, as well as the correlation coefficients ($R^2=0.9482$) of the Langmuir model is more suitable than the Freundlich model ($R^2=0.916$) for removing chromium from the wastewater using *swietenia mahagoni* bark adsorbent. The value of K_m obtained from Langmuir's model is negative (-24.2718) which indicates that low concentration of adsorbent cannot be explained by this model. The value of $1/n$ (0.28690) that is below 1 indicates that Freundlich model does not show favorable adsorption conditions for *swietenia mahagoni* bark adsorbent. There is a dynamic equilibrium existing between adsorbed and free molecules. Adsorption is

monolayer with a fixed number of vacant homogeneous adsorption sites.

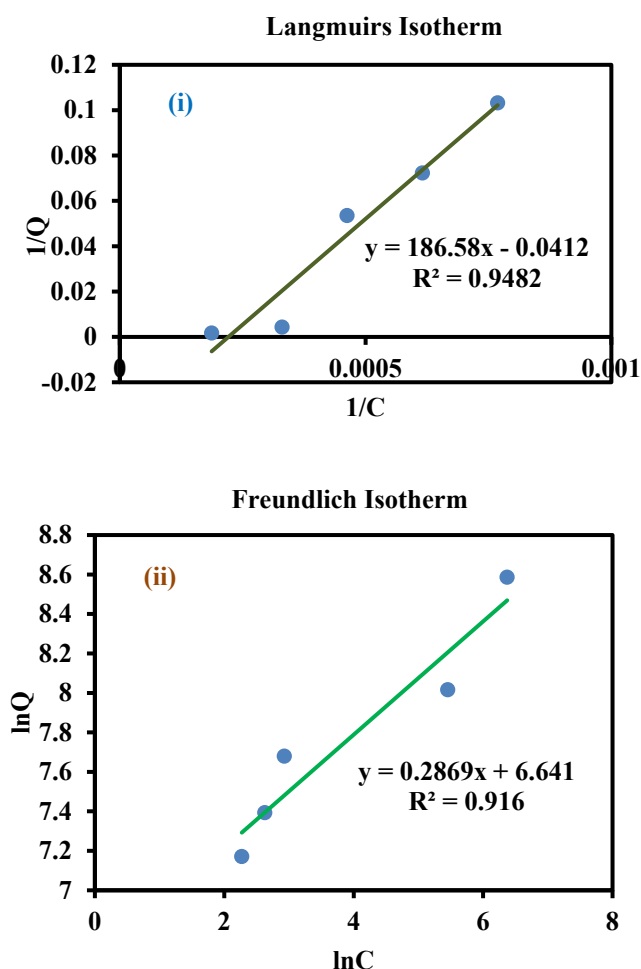


Fig.6: Adsorption isotherm: (i) Langmuir's isotherm (ii) Freundlich isotherm

3.7 Treatment process efficiency

The results of the treatment process with optimum conditions are represented in Table 1. The physicochemical parameters were obtained after all stages of treatments were: chromium 18.684 mg/L, pH 6.9, EC 84.1 mS, BOD 121(mg/L), and COD 289(mg/L). The highest percentage of chromium removal of chromium was 99.533%. It seems that after treatment pH, BOD, COD were within the discharged level although other parameters e.g. Chromium, EC were high from the discharge limit, but after treatment they have reduced to a noticeable amount. In batch-wise experiment a high percentage of chromium was removed from the tannery wastewater by *swietenia mahagoni* bark as bio-sorbent. In Table 1, the maximum percentage of chromium removal (99.533 %) in this study is compared with the chromium removal efficiency of other adsorbents used in some previous studies that shows a noticeable increment in chromium removal efficiency.

4. CONCLUSION

The current study analyze is a dynamic approach regarding chromium removal and new application as well from spent liquor of the tanning industry. Besides

that, *swietenia mahagoni* would be considered as cost effective bio-sorbent due to its huge availability. The *swietenia mahagoni* bark is capable of removing Cr from aqueous solution, up to 99.702%, adsorbent dosage of 3 g/30mL waste liquor. Chromium removal efficiency was increased with the increasing of adsorbent dose before reaching optimum point. 3g/30 mL dose of *swietenia mahagoni* bark bio-sorbent is the optimum dose which also decreases the amount of BOD, COD, and turbidity at a noticeable quantity. The removal percentage was increased with the increasing of contact time and the optimum contact time was found to be 15 minutes where 99.533% chromium had been removed. So removal of Cr from spent Cr liquor by *swietenia mahagoni* bark bio-sorbent could be a better option.

5. ACKNOWLEDGEMENTS

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