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Cost effective treatment of tannery effluent by alkali and *Azadirachta indica*

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Abstract

In this study cost effective remediation of tannery effluent was performed by alkaline treatment followed by filtration over neem leaves powder. The effluent was contaminated by deep blue color, distasteful odor, slightly basic pH, TDS, EC, COD, Cr and Cu. The Color, TDS, EC and COD were declined in a mentionable trend by alkali treatment in different pH, however, the concentration of Cr and Cu was unaffected. After filtration of alkali treated tannery effluent over *Azadirachta indica* powder, showed highly satisfactory removal efficiency for Cr and Cu. The removal efficiency of Cr and Cu ions over *Azadirachta indica* was 97 and 98 %, respectively.

1. Introduction

Industrial development is the key sign for the development of a country. Accompanied by industrial development many developing countries like Bangladesh ignore the environmental cleanness. Water pollution by industrial effluent carrying heavy metals (especially Cr and Cu) is a great concern for developing countries. The sewages from electroplating, tannery, coal combustion, metallurgical industries, paints, pigments, printing and graphics, mine production, waste disposal, agricultural waste and sewage are the main sources for chromium pollution [1]. The widely used industries for Copper are metal cleaning and plating, paper board, printed circuit board, wood pulp, fertilizer, paints and pigments [2]. Long term exposure of Chromium (total) causes allergic dermatitis. High concentration of Copper (II) ingestion causes stomach upset and ulceration, mental retardation, liver and brain damage [3]. The industrial and domestic wastewater is responsible for several damages of the environment and adversely affecting to the aquatic life, human health and ecosystem [4, 5]. Tannery effluent without prior treatment is a threatening metal pollution source for the Buriganga River of Bangladesh [4]. The Buriganga is a historical and commercially important River in Bangladesh flowing at the southern edge of Dhaka Metropolitan area. But from last couple of decades the Buriganga is polluted by effluents as a consequence of chrome tanning from tannery industries. Besides these, copper has been mixed with the Buriganga River water from tannery and other different copper discharging industries situated on the bank of Burigonga. Moreover, household wastewater directly discharges to the river through the pipeline made by copper. The people of Dhaka city and especially the people living on the bank of Buriganga are facing various health problems by using the polluted water directly or indirectly as the Buriganga is a major source of water for the nomad dwellers. Toxic Metals should be separated from other pollutants, since they are non-biodegradable and can accumulate in plant tissue and concentrated throughout the food chain [6].

Thus the removal of heavy metal from industrial effluent is one of the growing concerns for us. The commonly applied methods for the treatment of industrial effluents are by precipitation, ion exchange, electrochemical process, membrane processes and adsorption [3]. A number of research have been done to remove heavy metals from wastewater using activated carbon [7], silica, titanium dioxide, calcium carbonate [8], alumina [9], various nano-materials such as nano-metal oxide [10]**,** carbon nanotubes [11], nanozeolite composites [12], and others. However, most of these techniques have some drawbacks such as complicated treatment process, high cost etc. Adsorption is one of the most flexible and effective method for the refutation of heavy metal. This solves the problem of heavy metal contamination and purifies the wastage more economically viable pathway, especially if low cost and biodegradable adsorbents are used. In recent years adsorption is considered to be a much preferable technique [13, 14]. A number of such materials have been investigated, including coal, agricultural wastes and by products of rice mill [15-17]. Now-a-days, it is a growing demand to find out a locally available, low cost and efficient adsorbent for the removal of Cr and Cu from industrial and municipal waste. Neem (***Azadirachta indica***) is a well-known locally available plant in Bangladesh. This study focuses on the characterization of tannery effluent, alkaline treatment and the removal efficiency of Cr and Cu through filtration process using Neem leaves powder.

2. Material and Methods

2.1. Neem Leaves Preparation

The adsorbent material *A. indica* leaves were collected from Tarabo, Narayanganj near Dhaka city. After collection, the adsorbent materials were transported to the laboratory and washed three times with tap water after that three times by deionized water. Clean leaves were dried in sunlight for 72 hours. After sun drying the Neem Leaves were dried at 70 ± 5^{o}C for 48 hours in an oven and grind by a mortar for the preparation of Neem Leaves Powder (NLP). The grinds were sieved and a certain size (150 µm) was collected and stored in a plastic pot for further use.

2.2. Effluent Collection

After chrome tanning, the effluent is drained out into the Buriganga River. The sample was collected from kalunagar, in Hazaribagh during October, 2012. After collection some water quality parameters like color, odor, TDS, EC, pH were recorded instantly and the samples were transported to the laboratory as soon as possible. After that COD was measured in the laboratory. The collected sample was stored in refrigerator by adding 10 ml of 0.1 N HNO_3 per liter of effluent to prevent the growth of microbial bacteria. The sample was sealed to prevent air oxidation. Before doing any experiment, the sample was taken into room temperature.

2.3. Effluent Analysis

Color of the sample was observed through eye sight and odor was observed by sense. EC and TDS were measured instrumentally and COD was measured by condensation and potassium dichromate oxidation. Heavy metal concentration was determined by ‘SHIMADZU, AA-7000, Shimadzu Corporation, Japan’ model atomic absorption spectrometer.

2.4. Effluent Digestion for Metal Analysis

In a pyrex volumetric flask 100 ml of sample was taken for heavy metal analysis (Cr & Cu). After that 9.0 ml 1N concentrated HCl was added followed by 3.0 ml 1N concentrated nitric acid addition. The taken sample was heated in sand bath nearly to dryness in fume hood. The sample was then taken to the room temperature and deionized water was added to the sample up to the 100 ml. Thereafter, the sample was filtered through a nylon membrane filter (Whatman, pore size 0.8 µm, diam. 47 mm). Finally, they were preserved for the determination of Cr and Cu.

2.5. Effluent Treatment

The effluent sample was treated at three different pH (8, 8.5, 9) by adding NaOH at the temperature 28.0 ± 1.0 ^{o}C. The effect of alkali treatment was investigated for physicochemical water quality parameters. At optimum pH the effluent sample was filtered through *A. indica* powder for the removal of Cr and Cu. In between 2 cm supporting layer of glass wool, 2.0 g of NLP was packed in a pyrex column (15 mm diameter) for 300 ml effluent. The adsorption effect was observed for 10.4749 mg/L Cr and 2.445 mg/L Cu concentrated tannery effluent (TE). The study was conducted at room temperature (28 ± 2 ^{o}C) and pH of TE was 8.5 ± 0.2. A feed bucket was connected to the inlet of the filtration column with plastic tubing. The effluent was passed through NLP filtering column by gravimetric flow. After passing through the filtering column, the elluent was collected at every 1 minute interval for first 20 minutes and then 10 minutes interval up to one hour, 20 minutes interval for second hour and 30 minutes interval for third hour. The concentration of Cr and Cu in elluent was analyzed by using AAS.

2.6. Data Analysis

The percentage of adsorption of Cr and Cu was calculated according to the following equation 1:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_o is the influent metal ion concentration (mg/L) and C_e is the eluate metal ion concentration (mg/L). The correlation among EC, COD and TDS at different pH was established by SPSS (16.0 version) software.

3. Results and discussion

3.1. Alkali treatment

The physicochemical parameters of raw tannery effluent and Basic treated effluent are shown in Table 1. The raw tannery effluent was slightly basic (pH 7.4). The color of the raw tannery effluent was brown and acrid in smell. After basic treatment the effluent was almost colorless and bit acrid in smell. Electrical Conductivity was very high in raw effluent (16.96 mS) at 28 ºC. EC showed 20%, 55% and 51% removal capacity at pH 8, 8.5 and 9. That means the ionic mobility becomes the lowest at pH 8.5. This is may be occurred due to the co-precipitation as metal hydroxide. However, the effluent treated bellow and above of pH 8.5, the conductance value was increased as that condition was not suitable for co-precipitation as a result of metal hydroxide coagulation. Chemical Oxygen Demand showed higher value in raw effluent (3460 mg/L) and at 8, 8.5 and 9 pH represent 52 %, 73 % and 68% removal efficiency. Total Dissolve Solid value was 13350 mg/L in raw effluent whereas after alkaline treatment almost 30%, 70% and 70% removal performance were observed at 8, 8.5 and 9 pH, respectively. In raw effluent Chromium and Copper concentration were 10.475 mg/L and 2.445 mg/L, respectively. The alkali treatment was unable to remove Cr and Cu from effluent. At pH 8.5 all the parameters reached at the lower value. The supernatant effluent of pH 8.5 was used for filtration on Neem leaves powder.

Table 1: Physicochemical parameters of raw and alkali treated tannery effluent

Parameters	Effluent (7.4 pH)	Alkali treatment (pH)		
		8	8.5	9
Color	brown	Light brown	Almost Colorless	Almost Colorless
Odor	Acrid	Acrid	Bit Acrid	Bit Acrid
EC µS	16.96	13.43	7.55	8.20
COD (mg/L)	3460	1640	920	1089
TDS (mg/L)	13350	9360	4035	4030

The dependency of parameters with different pH has been established by Pearson's correlation. The value of EC, COD and TDS with different pH shows strong significant ($P < 0.01$) and negative correlation with each other (Table 2) which reveals that with increasing pH the concentration of parameters will be decreased. The change of r value in Pearson's correlation is slightly lower for COD ($r = -0.869$) compared to TDS ($r = -0.948$) and EC ($r = -0.928$) which rationalized the higher value of COD after alkali treatment (Table 1).

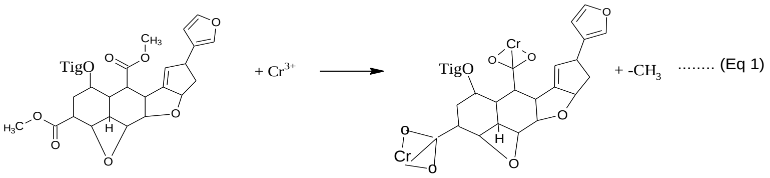
Table 2: Correlation among the alkali treated value

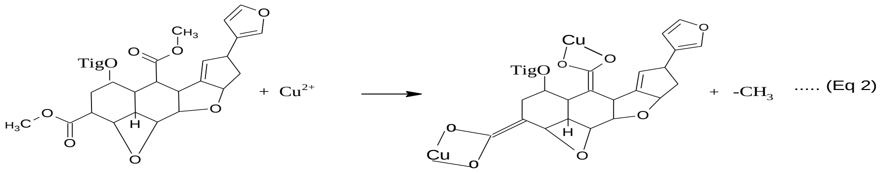
Parameters	pH	EC	TDS	COD
pH	1			
EC	-.928	1		
TDS	-.948	.997**	1	
COD	-.869	.934	.945	1

**Correlation is significant at the 0.01 level (2-tailed)

3.2. Characterization of Adsorbent

For FTIR study, each sample was mixed with KBr (1.0% w/w) and prepared pellets. KBr and sample were mixed by grinding in an agate mortar. FTIR spectra were recorded with IR-Prestige 21 (Shimadzu, Japan) spectrophotometer in the range 4000-400 cm^{-1}. The FTIR spectrum of *A. indica* before and after filtration is shown in Fig. 1. The OH band was found at 3439 cm^{-1}, the C-H stretch for methylene was found at 2924 cm^{-1} and 2851 cm^{-1}. C-O stretching vibration was observed at 1274 and 1064 cm^{-1} [18, 19]. Beside these, N-H band for amines spectrum was observed at 1630 cm^{-1} [20]. These bands are indicative of terpenoid group present in the Neem leaf [21]. $-CH_3$ band for alkanes was observed at 1437 cm^{-1}. C=0 stretching of carboxylic anion is observed at 1322 cm^{-1}. After adsorption most of the adsorption bands shift in the frequency with decreasing their intensity. The slight changes in the bands of FT-IR spectra of the NLP absorption peak due to the binding of the metal ions on the active sites of the NLP [22]. As a result of chemisorption, the band at 1322 cm^{-1} is disappeared and a new band at 1161 cm^{-1} is appeared after adsorption [23]. The spectra after adsorption obtained with decreasing the intensity indicated the physical adsorption. Asif M., (2013) [24], found, *A. indica* composed a chemical structure containing -$COOCH_3$ (NIM-76). Thereby, Cr^{3+} and Cu^{2+} may be reacted with the carbonyl groups and form -COOCr (Eq 1) as well as –COOCu (Eq 2). Hence, starching band of carbonyl group has been disappeared from the spectrum that was taken after adsorption.





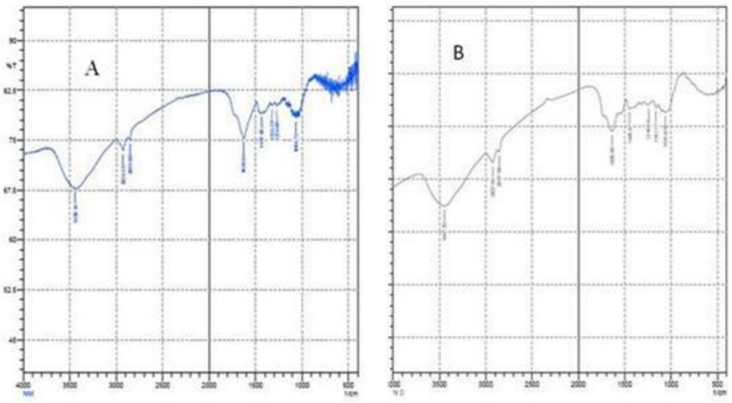


Figure 1: FTIR spectrum of *A. indica* leaves powder (A) before filtration (B) After filtration

3.3. Morphology

The SEM image was taken by an electron microscope (model-SSOQLD9111, Netherland) in 100 µm magnification. A hand pressured pellet was prepared by an apparatus for taking SEM image. The image is a flower like rough surface with edge and cavity. The rough surface morphology (Fig. 2) depicts that NLP is significantly useful for adsorption. There are a number of cavities were observed in the surface of NLP which form active site for efficient adsorption.

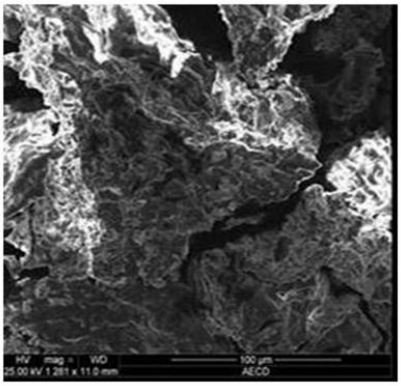


Figure 2: SEM image of Neem Leaf powder (*Azadirachta indica*)

3.4. Effect of time on removal

The removal of Cr and Cu from tannery effluent by filtration process is shown in Fig, 3. The experimental results reveal that the time has a strong effect on removal efficiency. Chromium and Copper both are shown the sharp removal efficiency up to 20 minutes. This higher rate of adsorption capacity with time endorsed the availability of more number of adsorption sites on adsorbent which play a vital role for the surface metal adsorption process [6, 25]. After certain time (20 min) the sharp removal efficiency has been decreased and the removal curve showed the almost flat trend although the removal continued up to 3 h. This is happened due to most of the available active site is occupied by the highly concentrated metal ion in effluent. Every adsorbent has a specific surface area which is not capable to adsorb any more ions after saturation. At the end of three hours the concentration of Cr and Cu in eluent was 0.28 mg/L and 0.05 mg/L, respectively. The concentration of Cr and Cu in eluent was in the permissible limit by Indian standard recommended value (2.0 mg/L Cr and 3.0 mg/L Cu) for industrial wastewater. Therefore, the eluent was safe for the discharging in the environment or nearest water body. The discharge water would not be harmful or burden for water ecosystem.

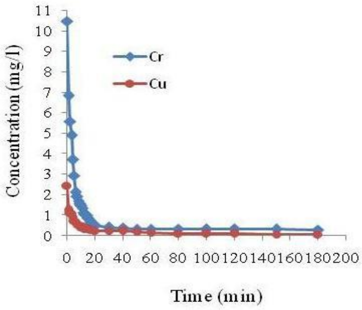


Figure 3: Effect of time on removal

3.5. Removal percentage

The removal percentage of Cr and Cu by neem leaves powder after alkali treatment is shown in Fig. 4. The time has a significant effect on removal percentage of Cr and Cu. In first 20 minutes 95.4 % Cr and 90.4 % Cu was removed from the effluent. After three hours period 97.3 % Cr and 98.2 % Cu was removed. This study reveals that after 80 min most of the adsorption sites become almost saturated and the removal percentage is also satisfactory as 97% and 96.5% for Cr and Cu, respectively. Therefore 80 min is enough for this adsorption process.

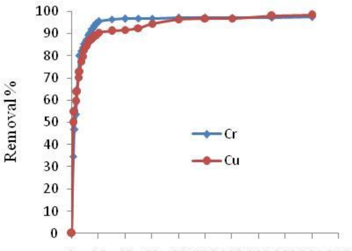


Figure 4: Effect of time on removal percentage

4. Economic and Environmental aspect of this experiment

Environmental issue is a great concern among the people of all over the world. Therefore, different chemical and physical process has been studied for the management of tannery effluent. Chowdhury et al., (2013) [26] reported that 96% Cr removal from tannery effluent after $FeCl_3$ treatment, Mandal et al. (2011) [27] showed that 23 % removal of Cr by H_2O_2 and $FeSO_4$ (Fenton oxidation) treatment. In coagulation process most commonly alum, $FeCl_3$, TiO_2, $MgSO_4$ and $NiSO_4$, H_2O_2 and H_2SO_4 are used as chemical. All the coagulation processes produce sludge and the removal of produced sludge from treatment plant is not easy to management which creates environmental problems. More over all the chemicals are expensive and are not eco-friendly. There are many studies used zeolites as ion-exchange resin for heavy metal removal but the experiment is on the laboratory scale. More work is needed for implementation for industrial scale [28]. Active carbon is mostly used for adsorption technique. However, active carbon is highly expensive for industrial use. In this study neem leaf powder was used as adsorbent. Neem leaf is a locally available low cost biomass which is biodegradable and environmental friendly. Beside this, there is no chemical treatment is necessary for satisfactory level of removal.

5. Conclusion

The main focus of this study is to establish a cost effective and locally available adsorbent for the tannery effluent treatment. The findings indicate that alkaline treatment could reduce certain amount of physicochemical parameters rather than trace metals (Cr and Cu). However, Cr and Cu could reduce by filtration process using Neem leaves powder. The removal capacity of Cr and Cu by filtration process using NLP was satisfactory without any pretreatment of adsorbent materials. This study depicts that 2.0 g raw NLP can remove about 97 % Cr and 98 % of Cu from tannery effluent (300 mL). Thus, NLP is a potential adsorbent which can be used by the small scale industries as alternative in the sustainable Cr and Cu removal technology for wastewater purification system.

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