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Investigation of Chloride Removal from Soaking Wastewater by Using Natural Biomass

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ABSTRACT
Soaking is the first beamhouse operation, where preserved hide/skin is rehydrated to make them flaccid, removal of dirt, and curing salt. The emitted soaking wastewater contains an enormous amount of dissolved solids. Common salt (NaCl) is mostly used for the preservation of hide/skin from which the primary pollutant chloride is emitted in the effluent. Due to its high dissolving capacity and non-biodegradability, chloride is difficult to remove. It has a detrimental effect on both aquatic and terrestrial ecosystems. Acute exposures to high levels of chloride have also been associated with diseases of the lower airways and interstitial lung. In this investigation, natural biosorbent *Tamarindus indica* leaf biomass was used to adsorb chloride from tannery-soaking wastewater. Batch-wise chloride adsorption from the soaking wastewater was performed considering different parameters-biomass dose, pH, and contact time. The biomass was characterized by the Fourier Transform Infrared (FT-IR) spectrum. The pseudo-second-order kinetics model was fitted to the chloride adsorption. The chloride content in the soaking wastewater before and after treatment was 18970.9 and 6306.9 mg/L, respectively. This treatment technique also reduced the pollution load: chloride, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), and electrical conductivity (EC) 66.8%, 44.07%, 39.57%, 29.63%, and 23.65%, accordingly from soaking wastewater. This investigation demonstrated the remarkable potential of *Tamarindus indica* leaf biomass to remove chloride from the soaking wastewater.

Keywords: Soaking wastewater, Chloride, Natural biomass, Biosorption, FTIR

1. Introduction
Bangladesh produces about 200 million square feet of leather annually making this industry an emergent contributor to its economy [1]. The leather industry is one of the most obnoxious and hazardous manufacturing sectors for generating excessive pollutants [2]. Manufacturing leather or leather goods from raw hide/skin includes a range of chemicals, resulting in a large amount of high-strength effluent. Every day 20,000m³ of tannery effluent and 232 tons of solid waste are generated [1].

The quality of collected raw hide/skin has a direct impact on the end product. Hence preserving the structural protein from microbial attack is crucial. Worldwide, the application of common salt to preserve raw hide/skin is the most practiced for its availability, low cost, and easy application. In the wet salting method, 40-50% of salt is applied to the flesh of the raw hide/skin. Salt creates an adverse condition for bacterial growth. However, this method generates 2.6 tons of salts in the initial unit operation, soaking [3]. The salt curing method produces TDS levels of over 70% and chlorides of over 40% [4]. Chlorides are responsible for permanent water hardness and decreasing the depth of the water column by bringing up sedimentation. They induce surface salt accumulation, causing excess soil alkalinity and infertility. They also pile up in the tissues of plants and influence the genotype [5]. Coagulation, precipitation, demineralization, ultra-filtration, nanofiltration, biological treatment, electrodialysis, adsorption, electrochemical, reverse osmosis, and solar evaporation are some methods used to lower the concentration of chlorides in the effluent. However, these techniques are mostly expensive and have certain negative environmental consequences [6].

Several dechlorinating procedures have also been tested including ion exchange, copper slag approach, and silver salt route [7-10]. Wang et al. [11] have used acid fermentation broth for the removal of chloride. Fang et al. [12] remove chloride ions from wastewater by using Friedel's Salt Precipitation Method. These approaches require high maintenance and expense. Bio-adsorption technique was applied as the biomass of *Parthenium sps.* which was able to reduce 40% of chloride content. *Polyalthia longifolia*, *Azadirachta indica* leaf powder, *Strychnos potatorum* seed powder, *Moringa indica* bark-based activated carbon are used for the removal of chloride [13-17]. Therefore, this investigation was an attempt to use biomass as an environmentally benign, cost-effective, and feasible biological agent to remove chloride from soaking effluent.

Indigenous to tropical, *Tamarindus indica* is a long-living species, widely distributed throughout the tropics, from South Asia to Africa. It has incredible medical properties consisting of different components of essential elements, phenolic substances, volatile components, organic acids, fatty acids, antimicrobial, antioxidative, anti-inflammatory, etc. activities [18]. Its leaf extract contains lupanone and lupeol which contribute to a diverse range of medicinal activities [19]. Hence, the usage of this leaf biomass is a sustainable, eco-friendly, and cleaner approach.

In this study, the biomass of *Tamarindus indica* leaf biosorbent was used to remove chloride from the soaking wastewater. Before and after use, the biosorbent was characterized through FTIR analysis. The adsorption isotherm and kinetics studies were performed.

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2. Materials and Methods

2.1 Sample collection

The soaking wastewater sample was collected in high-density polyethylene (HDPE) bottle from SAF Leather Limited, Jashore, Bangladesh. Before collecting the sample, the HDPE bottle was washed with diluted nitric acid according to the standard laboratory method and rinsed with distilled water several times.

2.2 Preparation of biomass

The *Tamarindus indica* leaves were collected from Rangpur, Bangladesh. The collected leaves were cleaned with distilled water to eliminate grime, dust, and other impurities. The leaves were sun-dried for two days, oven-dried at 105°C for 24 hours, pulverized using a laboratory grinder, and sieved on 80 meshes. The ground was stored in an airtight zipper for further use.

Fig.1 Prepared biomass of *Tamarindus indica* leaf

2.3 Reagents

The reagents-silver nitrate (Yingdashiji, China), potassium chromate, sodium hydroxide, ferroin indicator, potassium dichromate, potassium iodide, sodium azide, manganous sulfate (Loba Chemie, India), ferrous ammonium sulfate, starch (UNI-CHEM, China), nitric acid, sulphuric acid, and potassium hydroxide pallets (Merck, Germany) were used that were collected from a local scientific store in Khulna, Bangladesh.

2.4 Adsorption isotherm

Langmuir and Freundlich adsorption isotherms were investigated in this work. According to the linear isotherm model, Langmuir theory represents the partition mechanism of the adsorbate on the adsorbent (solid) and liquid phases [20]. Polar bonding, Van der Wall's interactions, and hydrophobic interactions all play a role in the interactions between the adsorbate and biomass [21]. The following equation is a linear expression of the Langmuir isotherm model.

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{1}$$

When the equilibrium concentration is C_e, q_e is the amount of adsorbate needed to create a single monolayer on a unit mass of adsorbent.

The Langmuir isotherm was used to calculate the non-dimensional separation factor (RL). The Freundlich model is one of the most prominent isotherms for representing nonlinear adsorption theory [22]. The following is a linearization of the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

Here, q_e represents the quantity of ion adsorbed per gram of adsorbent at equilibrium (mg g^{-1}); C represents the amount of ion concentration at time (mg/L); and K_F and n represent the Freundlich constants.

2.5 Adsorption kinetics

The first and second-order rate kinetics were determined using Elovich kinetics models [23]. Lagergren's basic pseudo-first-order equation for sorption is as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{3}$$

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \tag{4}$$

Where the second-order reaction rate equilibrium constant is K_2 (g mg^{-1} min^{-1}).

2.6 FTIR analysis

Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Nicolet iS5) in the range 4000 cm^{-1} to 400cm^{-1} was used to analyze the chemical linkages in the beneficiated biomass.

2.7 Monitoring of physicochemical parameters

A calibrated pH meter was used to measure the pH of the solution. APHA 2021 method was followed to determine the biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), and electrical conductivity (EC). The chloride was determined using the approved IS 3025 (Mohr's Method), which was reaffirmed in 2003.

2.8 Batch adsorption

The batch-wise assessment was carried out where the adsorption behavior of chloride on the biosorbent was studied under fixed conditions. The one factor at a time (OFAAT) approach was implemented to satisfy this objective. The influencing parameters were studied for batch adsorption-biosorbent dose, pH, and contact time. The effect of biosorbent dose intake was observed by changing the mass at 0.50, 0.75, 1.00, 1.25, and 1.50 g for 50 mL of wastewater for 5 minutes at 150 rpm. The pH was varying from 6.0, 7.0, 8.0, 9.0, and 10.0 and it was adjusted by using sodium hydroxide and nitric acid while other parameters were unchanged (dose 0.7 g, and 150 rpm). The contact times were changed to 30, 60, 90, 120, 150, and 180 min while other parameters were unchanged (dose 0.7 g, pH 8.0, and 150 rpm).

3. Results and Discussion

3.1 Effect of biosorbent dose

Figure 2 illustrates the effect of dose on chloride removal. At 0.5g biosorbent for 50 mL wastewater, the

percentage of chloride removal was low compared to other doses. This is because when a 0.5g dose was used, the Cl^- concentration of wastewater was higher, and the adsorption capacity of the biomass was low. With increasing biosorbent dose at 0.75g, the chloride removal percentage was increased to 66.83%. At the initial state, the surface of biomass was enough active to adsorb the chloride. While the biosorbent dose was increased to 1.0g, all the adsorbents were not worked properly because of the repulsive forces of the adsorbed chloride and the free chloride present in the solution. Hence, the removal percentage decreased. Adsorption capacity slightly increased to 63.48% when the dose was 1.25g.
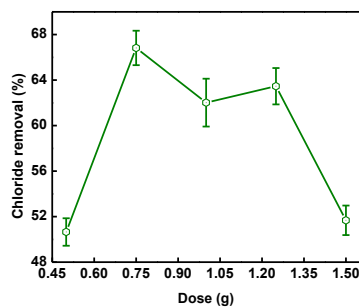

Fig.2 Effect of biomass dose on the removal of chloride

The chloride removal percentage increased only for 0.75g of biosorbent, due to an increase in the dose some re-adsorption capacity was restored, and the new active sites adsorbed some Cl^-. However, when the dose was increased to 1.5g, the removal percentage decreased to 51.68%. This was due to a lack of available Cl^- than the adsorbent. The gradual increase in doses did not recover the removal percentage. Therefore, it was decided that the highest chloride removal was achieved with 0.75 g biosorbent for every 50 mL of wastewater. But the highest chloride removal obtained in this study is comparatively lower than the other studies (Table 1).

Table 1 Comparison of the present study with other studies

Type of waste	Adsorbent source	% of Chloride removal	Reference
Tannery wastewater	*Tamarindus indica* leaves	66.8	This study
Textile wastewater	Banana fiber	70.94	[24]
Industrial wastewater	*Adansonia digitata* fruit	67.61	[25]
Desulfurization Wastewater	Fly ash	68.1	[26]
Domestic wastewater	Chitosan	63.2	[27]

3.2 Effect of pH optimization

Figure 3 represents the effect of pH on chloride removal from wastewater by using *Tamarindus indica*

leaf. During pH optimization, an identical dose (0.75g) was maintained. The effectiveness of chloride removal appeared to have increased with the pH raise. The chloride removal efficiency of biomass improved proportionally, and the apparent reason was, that as the pH rose, the number of active sites in the biomass rose, allowing the adsorption of chloride from the wastewater. Gradually decreasing the removal efficiency as the pores became saturated and the adsorbing capability of chloride was reduced. The surface was positively charged while pH was increased, and anions were less adsorbed as hydroxide ions increased. From the view of the adsorbent, the pH was below the pHpzc value, and the surface charge of the adsorbent would be positive so that the anions can be adsorbed.
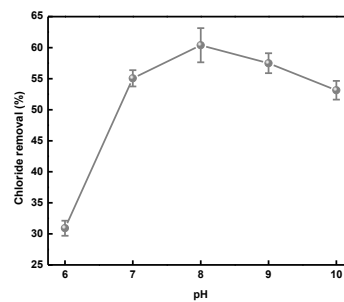

Fig.3 Effect of pH on the removal of chloride

3.3 Effect of contact time

Figure 4 portrays the chloride removal behavior as a function of retention time. Adsorption occurs on the adsorbent's exterior surface, due to its high attraction amid chloride and the adsorbent. At 30 min, chloride removal was 46.3% but at 60 min it was 41.2%. After that, it gradually increased and at 120 min was 53.3% then again decreased. With the increasing contact time to 150 min, the biosorbent lost its capacity to adsorb chloride. Thus, it was anticipated the maximum chloride occurred at a contact time of 120 min.
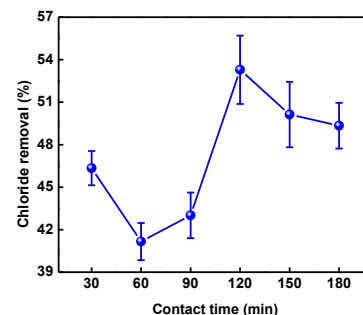

Fig.4 Effect of contact time (min) on the removal of chloride.

3.4 FTIR analysis

The equipped biosorbent was analyzed before and after treatment using Fourier Transform Infrared (FTIR) spectroscopy. Figure 5 depicts the FTIR spectrum of biosorbent before and after use. FTIR spectrum

differentiates the active components; functional groups detected in the leaf biosorbent. The adsorption bands of before treatment were 481 cm^{-1}, 603 cm^{-1}, 888 cm^{-1}, 1058 cm^{-1}, 1260 cm^{-1}, 1383 cm^{-1}, 1514 cm^{-1}, 1679 cm^{-1}, 2357 cm^{-1}, 3440 cm^{-1}. After treatment adsorption bands were 2916 cm^{-1}, 2847 cm^{-1}, 2377 cm^{-1}, 1634 cm^{-1}, 1539 cm^{-1}, 1449 cm^{-1}, 1240 cm^{-1}, 1178 cm^{-1}, 667cm^{-1}; assigned to various functional group stretching vibrations.
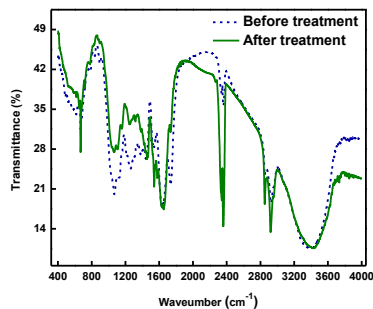

Fig.5 FTIR analysis before and after treatment of biomass.

However, the peak values 481 cm^{-1} and 3440 cm^{-1} remained unchanged which are for O−H (Alcohol or phenol), R−H (alkyl halide). But the other peak values changed their position while adsorption bands shifted at (603 to 667) cm^{-1}, (1058 to 1178) cm^{-1}, (1260 to 1240) cm^{-1}, (1383 to 1449) cm^{-1}, (1514 to 1539) cm^{-1}, (1679 to 1634) cm^{-1}, (2357 to 2377) cm^{-1}, and new peak values obtained in 2847 cm^{-1} and 2916 cm^{-1}, the functional groups in their stretching condition were CH$_3$−I, C−S, R−COO−R′, CH$_3$−CHO, CH$_3$−CO, NO$^+$, −CO, C≡N-, −C≡C−, C−H, −CH$_3$, =CH$_2$, ≡CH according to the FTIR spectrum. After using the biosorbent, some changes caused the adsorption on the surface. The main changes were in the functional group of −CH$_2$, −C≡C− and R−COOH, they showed peak values during adsorption and the adsorption occurred by hydrogen bond, electrostatic bond, polar bond, as well as chemisorption process. As a necessary consequence, it is apparent that the biosorbent adsorbed the chloride.

3.5 Adsorption Kinetics

3.5.1 Pseudo first-order kinetics

In comparison, the pseudo-first-order kinetic, the equilibrium value, and $R^2 = 0.5343$ were not satisfactory. The value K$_1$ was 5.96×10^{-5} min^{-1} and q$_e$ was 150.254 gL^{-1}. These showed the first-order kinetics was insufficient to describe adsorption kinetics. In addition, the R^2 value was low and fitting was not significant. Where the first-order rate equation is insufficient to describe the kinetics, second-order kinetics should be examined, since the lnq$_e$ value was not found to be equal to the intercept of the plot [28]. Figure 6, shows the graphical representation of pseudo-first-order adsorption kinetics.
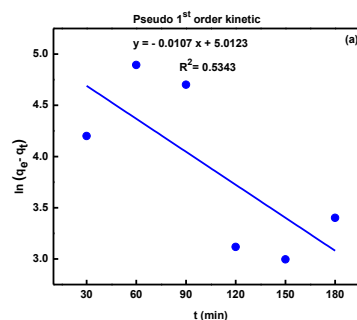

Fig.6 Pseudo first-order adsorption kinetics.

3.5.2 Pseudo second-order kinetics

For the applicability of second-order kinetics, a plot of t/q$_t$ against t (min), as shown in figure 7, yielded a linear relationship. The second order rate constant K$_2$ was found to be 1.36×10^{-4} gmg^{-1}min^{-1}, and a value of q$_e$ was 671.141mgL^{-1} which was much closer to the true q$_e$ value 640.704 mgL^{-1} of adsorbent. The $R^2 = 0.9810$ was close to 1. This meant the adsorption was governed by second-order kinetics. It seemed that the pseudo-second-order model described better adsorption kinetics for the adsorbents. This suggested the sorption of Cl$^-$ on the biosorbent and was most likely to be controlled by the chemisorption process [29].
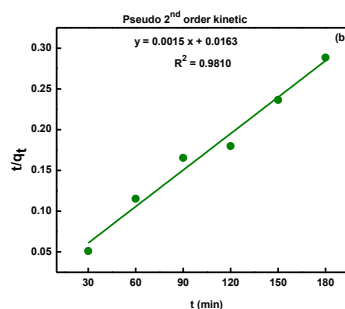

Fig.7 Pseudo second-order adsorption kinetics.

3.6 Adsorption isotherm

3.6.1 Langmuir isotherm

The Langmuir adsorption isotherm is appropriate when chloride is adsorbed as a single monocular layer onto the adsorbent. The isotherm is based on the equilibrium between the adsorbed chloride which exists in the liquid phase, with adsorption defined as the establishment of an ionic or covalent link between the biosorbent and the adsorbate. The isotherm plot in this study was linear, as shown in figure 8, showing that monolayer adsorption had occurred. The monolayer adsorption of Cl$^-$ on the adsorbent surface is validated by a good correlation coefficient (R^2=0.9756). The constant q$_e$ representing the adsorption capacity to produce a monolayer was as high as 425.53 mg/g of adsorbent. The separation factor R$_L$ is a dimensionless constant that describes the main characteristics of the Langmuir isotherm. The R$_L$ value calculated was 0.145. It was found to be in the range indicating the technique was well accepted.
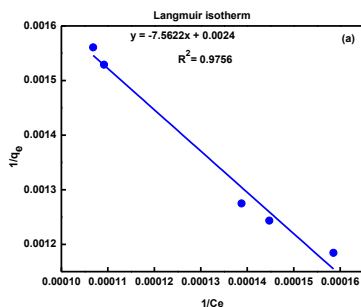
Fig.8 Langmuir isotherm for *Tamarindus indica* leaves adsorbent

3.6.2 Freundlich isotherm

The Freundlich equation is a unique and most important multi-site adsorption isotherm for rough surfaces; consequently, if the data fits the equation, it is only likely, but not proven, that the surface is heterogeneous. The heterogeneity of the surface can be confirmed with calorimetry. Heterogeneous adsorption (multi-site) has a variable ΔH of adsorption depending on the percent of sites occupied and chemisorption occurs [30]. This isotherm has two parameters while Langmuir's equation has only one; resulting, the former often fit the data on the rough surfaces better than Langmuir's equation. Freundlich adsorption isotherm is an empirical equation employed to describe the data for heterogeneous adsorbents [22]. A straight line was discovered when log q_e and log C_e were plotted. K_F denotes the biosorbent adsorption capacity toward the adsorption process whereas n denotes the level of surface heterogeneity and defines how the adsorbed molecules are distributed across the adsorbent surface. The estimated K_F value is 4.417×10^5 mg/g. The value of n was 1.4 in the investigation, which was more than 1, indicating the adsorption process was favorable [31]. In addition, the correlation coefficient ($R^2 = 0.9955$) exceeded the Langmuir isotherm. Figure 9 shows the graphical representation of the Freundlich isotherm.
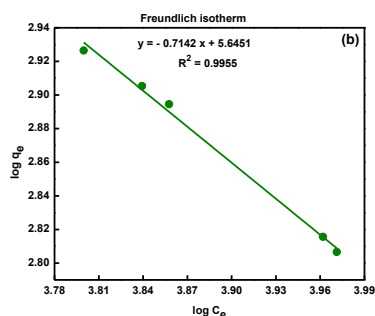

Fig.9 Freundlich isotherm *Tamarindus indica* leaves adsorbent

3.7 Characteristics of wastewater

Table 2 represents the characteristics of wastewater and the standard discharge limit of tannery wastewater. The chloride, TDS, EC, COD, and BOD_5 level was 31.6,

6.8, 26.2, 16.6, and 9.1 times higher than the standard levels. By using *Tamarindus indica* leaf biosorbent the removal efficiencies of chloride, COD, BOD, TDS, and EC were 66.8%, 44.07%, 39.57%, 29.63%, and 23.54%, respectively.

Table 2 Physiochemical parameters of soaking wastewater.

Parameter	Unit	Raw wastewater	Optimized wastewater	ECR (1997)
pH	-	8.4	8.0	-
Cl^-	mg/L	18970.85	6306.93	600
TDS	mg/L	14310.02	10070.01	2100
EC	mS	31.47	24.06	1.2
Salinity	ppt	18.20	8.9	-
COD	mg/L	6635.23	3710.85	400
BOD_5	mg/L	1824.13	1102.32	200

4. Conclusion

This investigation is a sustainable and cleaner approach by which chloride is removed from tannery-soaking wastewater using a biosorbent. The biosorbent as well as intraparticle diffusion plays a role in chloride adsorption. The chloride content in the raw wastewater and treated wastewater was 18970.85 and 6306.93 mg/L, respectively. The efficiency of biosorbent for chloride removal was 66.83%. Along with chloride removal treatment, the other pollution load e.g. COD, BOD, TDS, and EC were also removed by 44.07%, 39.57%, 29.63%, and 23.54%, respectively. Considering the potential of the process and the availability of the adsorbent, it can be implemented industrially with further cost analysis and input-output ratio.

5. Acknowledgement

6. References

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