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Chloride Removal from Tannery Soaking Wastewater by Adsorption onto Activated Alumina

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ABSTRACT
Tannery soaking waste water is characterized by very high chloride content that is responsible for severe environmental problems such as damage to human health, microbial population and aquatic lives. This study was aimed by the preparation and characterization of activated alumina along with its application for chloride adsorption from tannery soaking waste liquor. Activated alumina was prepared through sol-gel technique using aluminum nitrate as precursor with the pHpzc of 8.1. The XRD analysis revealed the both crystalline and fine amorphous nature of the alumina with average particle size of 5.04nm. Chlorides adsorption experiments onto activated alumina was conducted by both batch and column adsorption method to explore the optimal adsorption condition and to investigate the practical usability of the adsorbent. The batch study revealed that pH of 6 and temperature of 40 ºC was the optimal operational conditions for chloride adsorption onto activated alumina. In the column study, higher chloride removal was observed at lower flow rates, with a reduction in efficiency from 93.27% to 86.94% as the flow rate increased from 2 to 4 mL/min. Breakthrough curve analysis at different flow rates revealed that a comparatively higher break point of 270 minutes and 240 minutes was observed for lower flow rates, 2 and 4 mL/min, respectively, whereas at higher flow rates, 8 mL/min breakpoint was noticed at 150 minutes. Breakthrough curve modeling demonstrated that the column adsorption process followed the Thomas model of adsorption kinetics. Better regeneration of the alumina up to two wash cycles was achieved for alkali wash. The adsorption efficacy of activated alumina for chlorides, BOD and COD as 93.24%, 69.18%, 75.68% from raw soaking liquor and 43.19%, 32.23% and 38.69% from diluted soaking wastewater signifies its potentiality to adsorb not only chlorides but also organic pollutants from tannery effluent.

Keywords: Activated Alumina, Soaking Wastewater, Chlorides, Column Study, Adsorbent Regeneration.

1. Introduction

The leather processing industry is responsible for generating large amount of hypersaline wastewater in the soaking operation. After slaughtering, the hides and skins are collected and preserved with high amount of common salt to prevent further decomposition. Then soaking is the first and foremost tannery operation during leather processing. The soaking operation aims to prepare the hides/skins for subsequent processing by rehydrating the skin proteins, loosening the fibrous structure, removing curing salts, and cleaning the surface contaminants [1]. This soak liquor is enriched with inorganic hypersaline liquids containing total dissolved solids (TDS) of more than 35g/L, huge organic content as BOD and COD and very high level of chloride ions. This excess chloride level harms the ecosystem by affecting the growth of plants, aquatic life and microbial communities. Chlorides are also responsible for reducing crop yields in irrigated areas. Hence, proper discharge and removal of chloride ions are obligatory [2].

Chloride removal from wastewater is complicated due to its inorganic structure and high solubility level. Researchers have studied various treatment categories for the effective removal of chlorides such as ion exchange method, electro dialysis, chemical precipitation, biological process and so on. Most of the methods mentioned above are very costly because of the involvement of high-cost materials, high energy-consuming processes and the need for frequent maintenance [3].

Due to the operational simplicity and very high regeneration potential, adsorption is considered a very cost effective method for pollutant removal from wastewater [4]. Several adsorbent materials like activated carbon, ion-exchange resins and carbon nanomaterials are commonly used to remove chloride ions. However, the high investment cost creates complexity and swipes the interest in more affordable alternatives [5]. Activated Alumina (AA) nowadays catches the attention of many researchers as an adsorbent material because of its high porosity and surface area. The mechanical strength, enriched acid-base property, thermal stability and various functional groups have made it an ideal material for adsorbing diversified ions from waste liquor. Moreover, the simple process design and the need for very low energy enhance its cost-effectiveness in wastewater treatment applications [6]. Adsorption potential of activated alumina has already been studied by researchers for the removal of fluorides, heavy metals and dissolved organic content with the significant removal efficacy. In contrast chloride removal efficiency of the activated alumina has not yet been tested. Moreover in the previous experiments researchers used synthetically prepared adsorbate containing water to test the performance of activated alumina whereas in this research real wastewater generated in the soaking operation of leather processing was used for analysis [6-7].

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The main focus of this study was to explore the chloride removal performance of activated alumina as adsorbent material from tannery soaking waste liquor through the column adsorption process. Initially, the batch adsorption method was conducted to investigate the optimal adsorption conditions of the activated alumina that will help to design the column experiments. Thomas kinetics model was used to breakthrough curve modelling of the column study to find the maximum adsorption capacity and breakthrough time to ensure the effective column operation. Adsorption of different other pollution parameters in waste soaking liquor by activated alumina was also investigated. Adsorbent regeneration study by different washing agents for chloride removal was also explored. The physicochemical and morphological characteristics of the adsorbent were also explored using different analytical techniques and instrumental analysis.

2. Materials and Method

2.1 Materials

Tannery-soaking wastewater was collected in pre-cleaned plastic bottles from a reputed tannery in Jessore, Bangladesh. The reagents used to prepare activated alumina were Al $(NO3)_3$, liquid ammonia, starch solution, HNO_3 and paraffin oil. Different other chemicals such as NaOH, KI, NaN_3, $Na_2S_2O_3$, $MnSO_4$, $AgNO_3$, K_2CrO_4, Ag_2SO_4, $HgSO_4$, $K_2Cr_2O_7$, H_2SO_4 etc. were also used in various analytical test methods. All the chemicals were from Loba chemie, India and were purchased from a local scientific store in Khulna, Bangladesh.

2.2 Preparation and characterization of activated alumina

Activated alumina was prepared as outlined by RM Belekar and SJ Dhoble [7]. First, alumina sol was synthesized by mixing 0.1M aluminum nitrate and liquid ammonia with 4% starch solution as a surfactant. The sol was aged overnight, mixed with 1M HNO_3 and further aged for several hours at 70 ^{0}C for gel formation. The gel was then granulated into spherical droplets in a paraffin oil and 10% ammonia solution bath. Finally, crystalline-activated alumina was achieved by washing, drying, and calcination the gel at 500 ^{0}C.

The pH, ash content, and moisture content of activated alumina were measured following ASTM standards (D 3838-80, D 2866-94, and D 2867-99), and bulk density was measured using the tamping method. The yield of activated alumina was calculated as the percentage of alumina produced relative to the amount of $AlNO_3$ used. Point of zero charge (pHpzc) was determined from the plot of initial pH vs ΔpH of alumina. In these experiments, alumina solutions (0.1 g/20 mL) were prepared using 0.01M salt solution at different pHs ranged from 2 to 12. After shaking the mixture at 150 rpm for 24 hours, the final pH was measured and ΔpH was calculated.

2.3 Characterization of tannery soaking wastewater

Tannery soaking wastewater was allowed to settle for 3 hours in a sedimentation cone followed by filtration through a cotton cloth to remove large solids. Characterization was then done using standard test methods for chloride (4500B), BOD (5210B), COD (5220C), TDS (2540C), and TSS (2540D) as per APHA standards [8]. Conductivity and salinity were measured using a multi-parameter instrument (BOECO CT-676, Germany), while pH and turbidity were measured using a pH meter (EZDO 5011, Taiwan) and turbidity meter (HACH 2100Q, USA), respectively. The treated wastewater after column study for the flow rate of 2mL/min was also characterized by following the above mentioned method for analysis.

2.4 Batch study for process optimization

Initially batch adsorption study for chloride removal by activated alumina was performed to optimize the pH, temperature and initial concentration of chlorides which will be maintained in the column study. The influence of pH and temperature on the adsorption process was tested by maintaining their ranges from 3 to 11 and 20 ^{0}C to 60 ^{0}C with the effluent volume of 50 mL having chloride concentration of 100 mg/L and adsorbent dosage was used as 0.3g. For the study of concentration optimization batches with the size of 50 mL were made from 10 to 100 mg/L of initial chloride concentration. All the experimental batches were stirred in magnetic stirring machine for 1 hour at 150 rpm. After the contact time the mixtures were allowed to settle undisturbedly for 1 hour, filter through 0.45 µm filter paper and residual chloride content was measured and percentage removal was calculated. Each experiment was conducted in triplicates and average value was used for analysis.

2.5 Column adsorption study

Column studies were conducted using three flow rates (2, 4, and 8 mL/min) with a bed height of 4.1 cm with 8.16 g of activated alumina. Wastewater was passed through the column at optimal conditions determined by the batch study, and filtered samples were collected at intervals from 30 to 510 minutes. Residual chloride was measured, and percentage removal was calculated for breakthrough curve analysis and modeling. Treated wastewater was characterized for various parameters and a comparison was made with the untreated water. Another column study was also conducted with the raw soaking wastewater directly without maintaining chloride concentration to desired level and different parameters of the untreated and treated water were compared as mentioned earlier.

2.6 Regeneration Study of the Adsorbent

The regeneration study was conducted by washing the used alumina with 0.1N NaOH, 0.1N H_2SO_4 and distilled water. After filtering and drying at 105 ^{0}C, the alumina was tested for chloride adsorption in batch method at optimal pH and temperature. The same procedure was repeated for three regeneration cycles. Percentage regeneration was calculated based on chloride removal in each cycle compared to the initial batch experiment.

3. Results and Discussion

3.1 Physico-chemical characteristics of activated alumina

The physicochemical features of the synthesized activated alumina are shown in Table 1 representing that prepared white colored activated alumina was alkaline in nature (pH 8.8) with Low apparent density 0.55 g/cn^3 suggesting the dense porous structure suitable for adsorption applications. Moisture content, 6.9% suggests the stability and durability of the alumina against microbial growth and its prevention from potential decay. The ash content, 16.45% represents the presence of high inorganic content in the product such as aluminum which plays the vital role in the adsorption process. Moderate yield value (10.15%) reflects that there is a scope for process improvement to minimize material losses.

Table 1 Physicochemical parameters of activated alumina

Parameters	Values
Yield (%)	10.15
pH	8.8
Color White	White
Moisture content (%)	6.9
Apparent density (g/cm^3)	0.55
Ash content (%)	16.45

3.2 pHpzc of the activated alumina

Point of zero charge (pHpzc) defined as the pH of the suspension at which the net surface charge of the adsorbent or catalysts is zero. This parameter is very significant for surface characterization of adsorbents along with the explanation of the adsorption mechanism of the adsorbents [9]. Fig. 1 represents the pHpzc plot of the activated alumina.

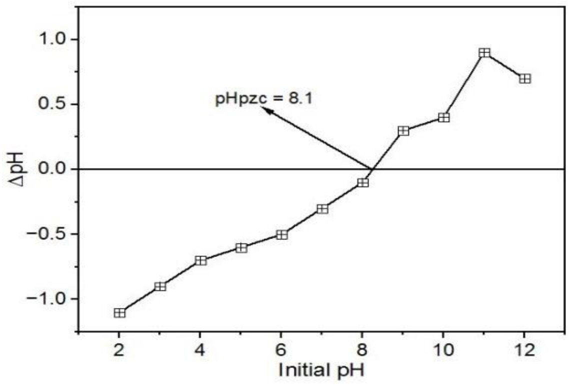

Fig. 1 pHpzc plot of the activated alumina

It is observed from the above figure that the zero line of ΔpH passed through pH 8.1, so it is considered as pHpzc of the activated alumina. pHpzc value indicates that if the pH value of the alumina suspension remains below 8.1, the surface gets a positive charge due to the protonation of surface hydroxyl groups. On the other hand, upon the increase of pH above 8.1, the surface of the alumina carries a negative charge due to the deprotonation of those groups.

3.3 XRD analysis

XRD analysis was conducted using a wide-angle X-ray diffractometer (Smart Lab SE, Rigaku, Japan) with Ni as the filter and Cu-Kα as the light source. The scans were recorded in the 2θ range of 20-80.

The 2θ versus intensity plot of the XRD data of the activated alumina given in Fig 2 represents that both sharps and relatively broader peaks are located in the XRD graph of the activated alumina. This kind of peak shape represents the crystallinity, fine size and amorphous phases of the activated alumina. The maximum intensity at the 2θ value of 66.90^0 of the synthesized alumina meets the reference XRD data of the activated alumina [10]. Other sharp peaks were observed at 2θ values of 37.44^0, 39.55^0 and 45.83^0, while broader peaks were noticed at 2θ of 60.72^0 and 35.26^0. The broader peaks in the XRD pattern represent the small crystalline grains and compositional fluctuations. The average crystallite size was calculated as 5.04 nm.

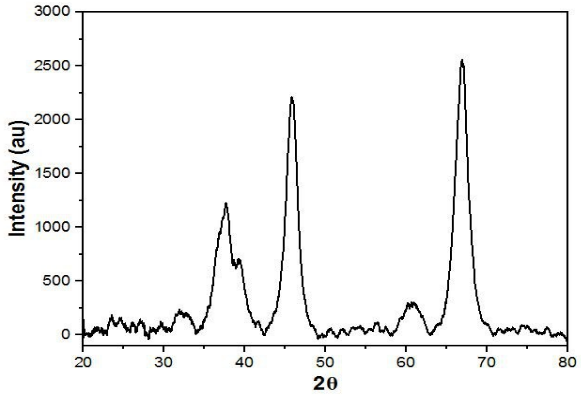

Fig. 2 XRD plot of the activated alumina

3.4 Study of batch adsorption process

3.4.1 Effect of pH on chloride removal

The influence of pH on the removal of chlorides by adsorption onto activated alumina was illustrated by the removal (%) vs pH plot, shown in the Fig. 3.

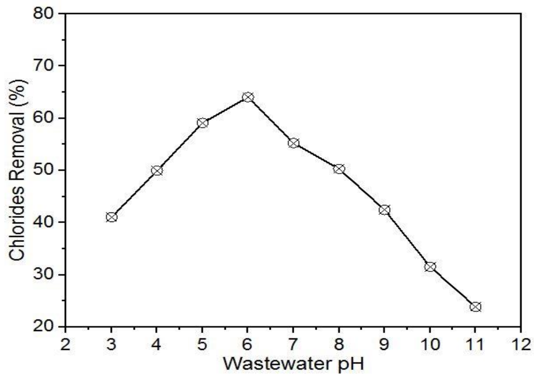

Fig. 3 Effect of pH on Chloride removal

It is observed from the above figure that chloride removal (%) increased with the increase of pH, reaching the maximum (64.05%) at pH 6. After that, the removal percentage started to decrease. The fall of chloride removal after pH 6 signifies that near and after the pHpzc (8.1) of alumina, the protonated surface sites (major sites for chloride binding) decreased. Similar observations were made by Yulin Tang and his research group regarding the adsorption of fluorides onto activated alumina. In this research, the adsorption maxima were between pH 5.5 to 7.5 [11]. Chloride removal was further decreased below the optimum pH, which may be because of the decrease in the availability of binding sites due to excess protonation or due to the competition of other anions in the liquor. The lowest removal of chlorides (23.86%) was noticed at pH 11. The optimum pH was identified as 6 in this test conditions.

3.4.2 Effect of temperature on chloride removal

The chloride removal (%) versus wastewater temperature graph in Fig. 4 illustrates the influence of temperature on the adsorption process. From the figure it is observed that as the temperature increases from 20°C, the chloride removal efficiency improves, reaching its peak with a highest removal of 71.58% at a temperature of 40 ^{0}C. After that when the temperature goes above 40°C, the removal efficiency significantly decreased, dropping to 29.12% at

60°C. This decline was likely due to desorption of chloride ions from the adsorbent surface at higher temperatures caused by the increase in kinetic energy of ions that weakens the interactions between the adsorbent and adsorbate [11]. Here, the increase in temperature up to 40 ^{0}C enhances the removal process, likely by accelerating physical or chemical interactions between adsorbate and adsorbent as desired. Temperature, 40 ^{0}C was selected as optimum.

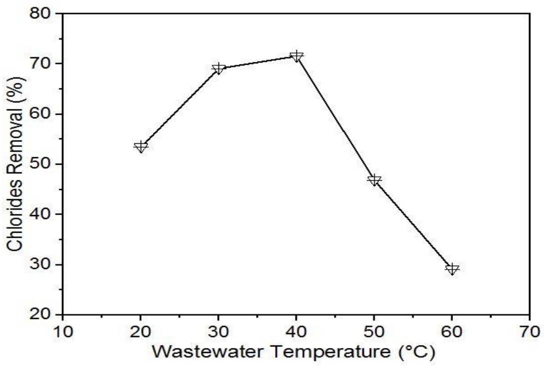

Fig. 4 Effect of temperature on chloride adsorption

3.4.3 Effect of concentration on the adsorption process

The impact of initial chloride concentration on the removal process is presented in Fig. 5.

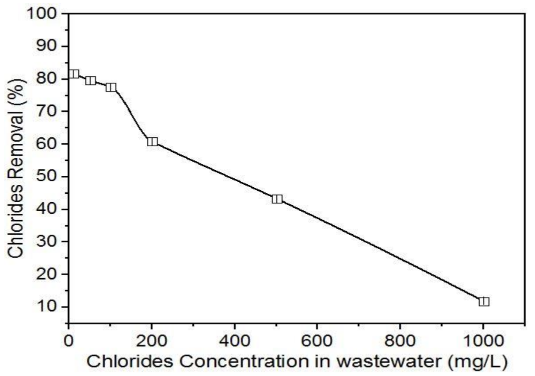

Fig. 5 Influence of chloride concentration on removal

The graph illustrates that for the initial concentration ranging from 10 to 100 mg/L the removal of chlorides decreased slowly with the removal percentages of 81.71%, 79.63% and 77.58% for 10 mg/L, 50 mg/l and 100 mg/L respectively. At the higher initial concentration beyond these, the removal efficiency decreased significantly with the minimum 11.18% removal of chlorides at a concentration of 1000 mg/L. The adsorption efficiency decreased at higher initial concentrations because the adsorption sites became saturated and the equilibrium was established [12]. By decreasing the initial chloride concentration from 100 mg/L to 10 mg/L, only 4.13% extra removal was achieved. So, considering the economical point of view in respect to the use of pure water for dilution of soaking liquor to desired concentration, initial chloride concentration of 100 mg/L was chosen in the column study.

3.5 Column study for chloride adsorption

3.5.1 Chlorides removal at varying wastewater flow rates

The Fig. 6 illustrates the influence of wastewater flow rates on chloride removal.

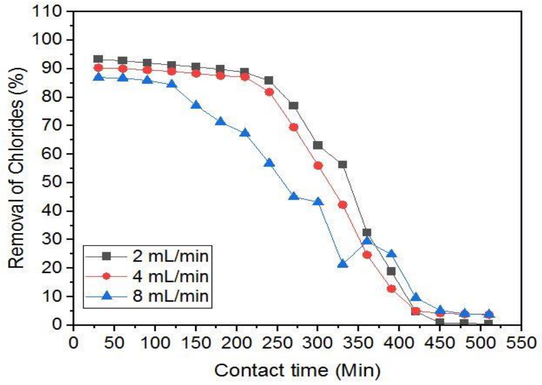

Fig. 6 Chloride removal at varying wastewater flow rate

It is observed from the Fig. 6 that as the flow rate increases, the percentage of chloride removal decreased. After 60 minutes, the chlorides removal was 92.81% for 2 mL/min, 90.04% for 4 mL/min, and 86.74% for 8 mL/min of flow rates. Removal performance decreased to below 50% for flowrate 2mL/min at a time of 360 minutes, for flow rate 4mL/min it was 330 minutes and the time was 270 minutes for flow rate of 8 mL/min. This trend suggests that higher flow rates lead to less efficient chloride removal, likely because the wastewater spends less time in contact with the treatment system and the speed of water in the column accelerates the desorption process.

3.5.2 Breakthrough curve analysis of the column study

The plot of contact time versus initial chloride concentration to residual concentration of chlorides after different time intervals was regarded as the breakthrough curve of chloride removal. The breakthrough plot is shown in Fig. 7.

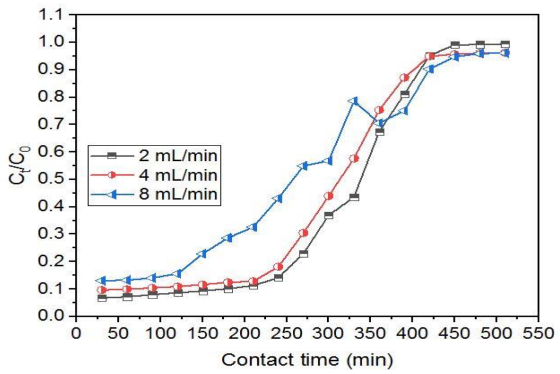

Fig. 7 Breakthrough plot of column study

The curve in the Fig. 7 illustrates the influence of flow rate on adsorption performance. There is an inverse relation between flow rate and breakthrough curve; as the flow rate increases the break point in the curve decreases because of the shorter time of the pollutants in the column, so the adsorption equilibrium affected largely at very high flow rate [12]. In this study at lower flow rate of 2 mL/min, there was more contact time between activated alumina and chlorides, the breakthrough occurred much later (break through point ,270 min) leading to better removal. The slope was also gradual, indicating efficient adsorption. As the flow rate increased to 4 mL/min the breakthrough time decreased and it was the lowest at the highest flow rate, 8mL/min (breakthrough point, 150 min). As the flow rate increased, the saturation period gets shorter while a lower flow rate extends the time to saturation.

3.5.3 Breakthrough Curve Modeling by Thomas model

Thomas kinetics model is linked with breakthrough curves and assesses adsorption efficiency that often serves as a primary stage in the design of a reducing system for the fixed-bed column [13]. The linear Thomas equation is represented as following.

$$\ln(\frac{C_0}{C_t} - 1) = \frac{k_{Th} q_{Th} m}{Q} - k_{Th} C_0 t \quad (1)$$

Where, t is total flow time (in minutes), m is mass of the adsorbent (measured in grams), Q is the flow rate (measured in mL min^{-1}). Using the data of the breakthrough curve, from the plot of the time (t) versus ln (c0/ct-1), different parameters of the Thomas's model were calculated. Thomas plot is shown in the Fig. 8 and the calculated parameters are given in the Table 2.

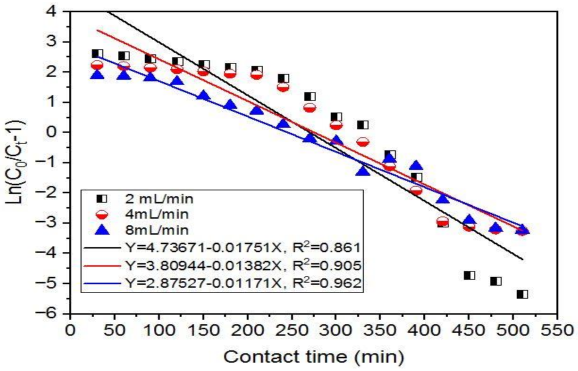

Fig. 8 Plot of the Thomas model

The coefficient of determination R^2 values for different flowrates was near and above 0.9 signifies that the experimental data fitted to the Thomas model. When the flow rate increased from 2 to 8 mL/min, the mass transfer coefficient (KTh) decreased from 0.000350 to 0.000234 $L \cdot mg^{-1} \cdot min^{-1}$, showing a clear inverse relationship between K_{Th} and flow rate. This was due to the fact that at higher flowrate, adsorbent and adsorbate get less time for adsorption and diffusion. The adsorption capacity q_{Th} values (12.04, 6.75 and 3.32 mg/mg) also decreased with flow rates, indicating more efficient chloride adsorption at lower flow rate. The faster flow rates reduced the contact time, which could limit adsorption.

Table 2 Parameters of the Thomas model

Parameters	**Flow rate 2mL/min**	**Flow rate 4mL/min**	**Flow rate 8mL/min**
kTh (Lmg-1min-1)	3.5×10^{-4}	2.76×10^{-4}	2.34×10^{-4}
qTh (mg/g)	12.04	6.75	3.32
R^2	0.861	0.905	0.962

3.6 Characteristics of the Tannery Soaking Wastewater

The Physico-chemical features of the raw and treated tannery soaking liquor by adsorption onto activated alumina are shown in Table 3.

Values in the Table 3 represent that tannery soaking liquor was highly saline and conductive in nature due to the presence of very large extent of TDS (14500 mg/L) and chloride content (11203 mg/L). Very low biodegradability of the waste liquor was reflected by its low BOD/COD (0.35) value. Wastewater characteristics improved greatly upon dilution (dilution factor-100) such as chlorides, TDS, BOD and COD content was changed to 1125 mg/L, 1472 mg/L, 331 mg/L, and 1024 mg/L respectively. After column treatment by activated alumina, different waste parameters along with chlorides removed significantly form the diluted soaking liquor such as chlorides (93.27%), TDS (78.19%), BOD (69.18%) and COD (75.68%) to the residual concentration of 76, 321, 102 and 249 mg/L respectively. A similar column treatment study with raw soaking wastewater revealed that notable removal of the waste parameters was observed, although to a lower degree in comparison with the diluted sample. Removal percentages of chlorides, TDS, BOD and COD were 22.39%, 43.19%, 32.23% and 38.69% with the residual concentration of 11254, 6364, 1022 and 2643 mg/L respectively. All the experiments explored that activated alumina is a potential adsorbent not only for chlorides but also for organic pollutants and other TDS components in tannery wastewater.

Table 3 Characteristics of raw and treated wastewater

Parameters	Values for raw soak liquor		Values for treated soak liquor	
	Undiluted	Diluted	Undiluted	Diluted
pH	9.4	8.3	7.9	6.7
Salinity (ppt)	16.3	2.36	11.43	0.67
Conductivity (mS)	25.26	5.18	19.87	1.03
Turbidity (NTU)	685	485	372	109
TDS (mg/L)	14500	1472	11254	321
TSS (mg/L)	3800	467	2038	138
Chlorides (mg/L)	11203	1125	6364	76
BOD_5 (mg/L)	1508	331	1022	102
COD (mg/L)	4311	1024	2643	249
BOD/COD	0.35	0.35	0.39	0.41

3.7 SEM analysis

SEM analysis of both raw and chloride-loaded alumina was done with a benchtop SEM (JCM 700, JOEL, Japan) after gold-coating with a sputtering device. SEM images of the alumina are given in the Fig. 9.

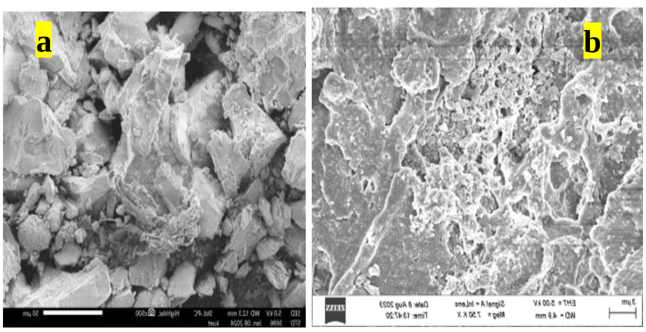

Fig. 9 Morphology of activated alumina (a = Raw alumina, b = Chloride loaded alumina)

The SEM image of the freshly prepared activated alumina (Fig. 9a) show that particles vary from irregular to nearly spherical shapes, characterized by a rough surface and numerous pores. This porous morphology facilitated high surface area, enhancing its adsorption capacity. In contrast, the SEM image of the chloride loaded alumina (Fig. 9b) showed aggregated clusters with a smoother and less porous surface, suggesting that chloride ions adsorbed effectively by occupying the alumina's pore structure.

3.8 Regeneration study of the activated alumina.

Experimental data of the regeneration study of activated alumina is represented in Fig. 10.

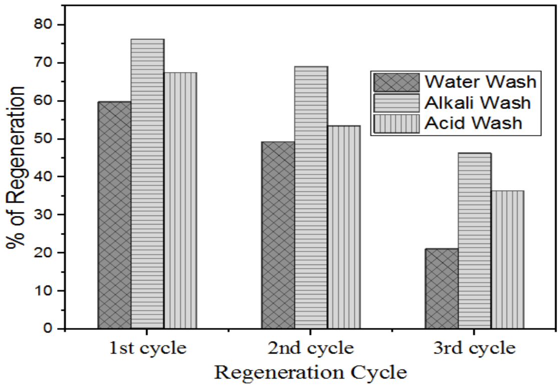

Fig. 10 Regeneration (%) of activated alumina

It is observed from the Fig. 12 that significant regeneration of adsorbent was achieved in the first and second cycle with alkali wash leading the top having the regeneration percentages of 76.24% and 69.28%. This suggested that the alkali wash was the most effective at restoring the adsorbent's capacity likely due to its ability to neutralize and remove adsorbed contaminants more thoroughly. By the third cycle, the regeneration efficiency declined for all methods signifying that the pore structure of the adsorbents may get degraded significantly.

4. Conclusion

Activated alumina as an adsorbent showed significant removal efficiency of chlorides from tannery waste soak liquor. At the optimal operational conditions, maximum removal of chlorides was achieved as 93.27% for the flow rate of 2 mL/min in the column adsorption process where highest break point as 270 minutes was noticed. Thomas kinetics model revealed that chloride adsorption capacity of alumina was 12.04 mg/g with the mass transfer coefficient of 0.000350 for the flow rate of 2 mL/min signifying that the more efficient adsorbate transfer to the adsorbent surface than other flow rates. Effective regeneration of the alumina was observed at first two cycles where alkali wash was the best option with the regeneration efficacy of 76.24% and 69.28%. This adsorption process improved the biodegradability of the wastewater such as BOD/COD ratio was 0.35 before treatment that was increased to 0.39 and 0.41 for the undiluted and diluted soak liquor. Activated alumina was a potential adsorbent for the adsorption of chlorides, other TDS and organic content from tannery wastewater.

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