

Removal of Chromium(III) and Other Physical Parameters from Chrome Tan Wastewater and Recovery of Chromium from the Precipitating Sludge

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ABSTRACT

This study was adopted to investigate the removal of Cr(III) and other physicochemical parameters of chrome tan wastewater. For this purpose, three precipitating agents, CaCO₃, NaHCO₃, and MgO, were used to treat chrome tan wastewater. After treatment, it was found, in three different dose trials, that each agent removed almost 97-99.5 % of chromium. At the same time, it was observed that with the increase of doses, removal percentage of TDS, conductivity, and turbidity of effluent were reduced. In the case of NaHCO₃ and CaCO₃, Cr(III) removal percentage at optimum pH was found to be 99.97% and 99.95% respectively, whereas the maximum removal percentage for MgO was found to be 99.98%. The NaHCO₃ and CaCO₃ were found to be comparable to MgO for Cr(III) removal from chrome tan wastewater. The recovered chromium concentration in the sludge for NaHCO₃ and CaCO₃ were also similar to that of MgO. This research suggests that these two precipitating agents can be used in the same way as MgO, for Cr removal and recovery treatments. Moreover, this recovered chromium can be reused, thus reducing the environmental pollution.

KEYWORDS

Chromium, precipitation, wastewater, environment, pollution

INTRODUCTION

Tanning is the process in which raw, putrescible hides and skins are converted into durable, non-putrescible leather [1]. It is one of the most critical steps in the leather industry towards preserving leather from microbial decay, heat, sweat and humidity [2]. It is reported that one ton of wet salted hide can yield only 200 kg of leather and consequently more than 50m³ of wastewater [3,4]. Chromium compounds are widely used in various industrial operations such as textile dyeing, electroplating, wood preservation, pigmenting, paper and leather industries. The pollutants resulting from these industries contain a large amount of untreated chromium, which is harmful for the environment [5,6]. Chrome tanning was introduced in the 19th century and it has been estimated that almost 90% of world leather production today is the result of chrome tanning [7,8]. In tanning process mainly trivalent chromium is used, unfortunately only 60% to 70% of chromium

reacts with collagen and the spent liquor i.e. the chrome tan wastewater contains remaining 30% to 40% of chromium [9]. Tanning processes have been developed based on salts of different metals though, for instance aluminium [10], sodium [11], titanium [12], iron [13]. Chromium is used in the tanning industry because the chrome-tanned leather has a high thermal stability and excellent physical properties. Currently, 6.5 million tons of raw hides and skins are made into leather worldwide. Solid waste consists of 56-60 % of fleshing, 35-40 % of chrome shaving, chrome split or buffing dust, 5-7 % of skin trimmings and 2-5 % of hair [14]. Depending on the chrome tanning process, chrome shaving dust in solid waste may contain 2.5 to 5 % of chromium (mostly trivalent chromium) [15,16]. Several researches suggested that wastewater contains 2500 ppm to 8000 ppm and 1300 ppm to 2500 ppm of chromium respectively [17,18]. The major chemical pollutants that come out from the tanning industry are sulfide and chromium; these chemicals spread into the local environment, which makes it harmful for the environment [19]. In Bangladesh, the soil and river water environment is highly affected by the tannery industries, which dramatically distort the ecological balance [20]. The permissible limit (EEPA) of chromium in wastewater is 2 mg/l for trivalent and 0.5 mg/l for hexavalent chromium [21]. A little amount of chromium is necessary for glucose, lipid and protein metabolism of mammals but long-time exposure can lead to various adverse health effects.

There are several methods of removal of chromium from the wastewater, like electrochemical precipitation [22,23,24], cation exchange membrane [25], solvent extraction, coagulation, membrane process and filtration [26], ion exchange [27,28] and adsorption [29-33]. With the exception of the precipitation method, most of the purification methods are costly in terms of installation and maintenance. However, this separated chromium recovery is also difficult and costly as well. Research has shown that CaCO_3 has potential to be used in Cr(III) and Ni(II) removal [34]. The MgO is already popular as a precipitating agent [3]. The NaHCO_3 also has potential to be used as a precipitating agent since it is already available in tanneries as a neutralizing agent [35]. In our study, NaHCO_3 , MgO and CaCO_3 have been used as precipitation agents to remove chromium from chrome tan wastewater due to high alkalinity, solubility, low cost and availability. The novelty of this study is that this research has not only shown the chromium removal efficiency of these precipitating agents, but has also made a comparison between the precipitating agents based on their chromium recovery efficiency. Many studies have already described the removal efficiency of several precipitation methods using different alkaline like NaOH, Ca(OH)_2 , MgO etc. [3]. However, there is very limited data on the recovery efficiency of the precipitating agents. After chromium removal from the chrome tan wastewater, the residual chromium in the precipitate should be re-used rather than be released into the environment. Therefore, it is necessary to evaluate the recovery efficiency along with the chromium removal efficiency of every chemical precipitation methods. It is also important to mention sludge characteristics, as it will also be released into the soil and the environment. It is an innovative approach of using alkalis like NaHCO_3 , CaCO_3 and MgO to compare their chromium removal efficiency along with the chromium recovery potential from the respective sludge obtained. Due to the high alkalinity and solubility as well as cost and availability, NaHCO_3 and CaCO_3 have a lot of potential to be used as precipitating agents in place of MgO. The aim of this study is to find out the potential of the mentioned precipitating agents for chromium removal from chrome tan wastewater and to evaluate their effects on the recovered sludge.

EXPERIMENTAL

Materials and Methods

Collection of Effluent

The spent liquor from the chrome-tanning drum was collected from Samina Tannery, located at tannery estate at Hemayetpur, Savar, Dhaka, Bangladesh and stored in pre-treated high-density polyethylene (HDPE) bottles. The spent liquor of the chrome tanning operation was collected just after the chrome tanning was finished. HDPE bottles were pre-treated with 0.5 M HNO₃ to remove any possible pollutant in the bottle and to retard any possible oxidation reaction. After that, all of the samples have been stored in a refrigeration system at 4°C before further analysis.

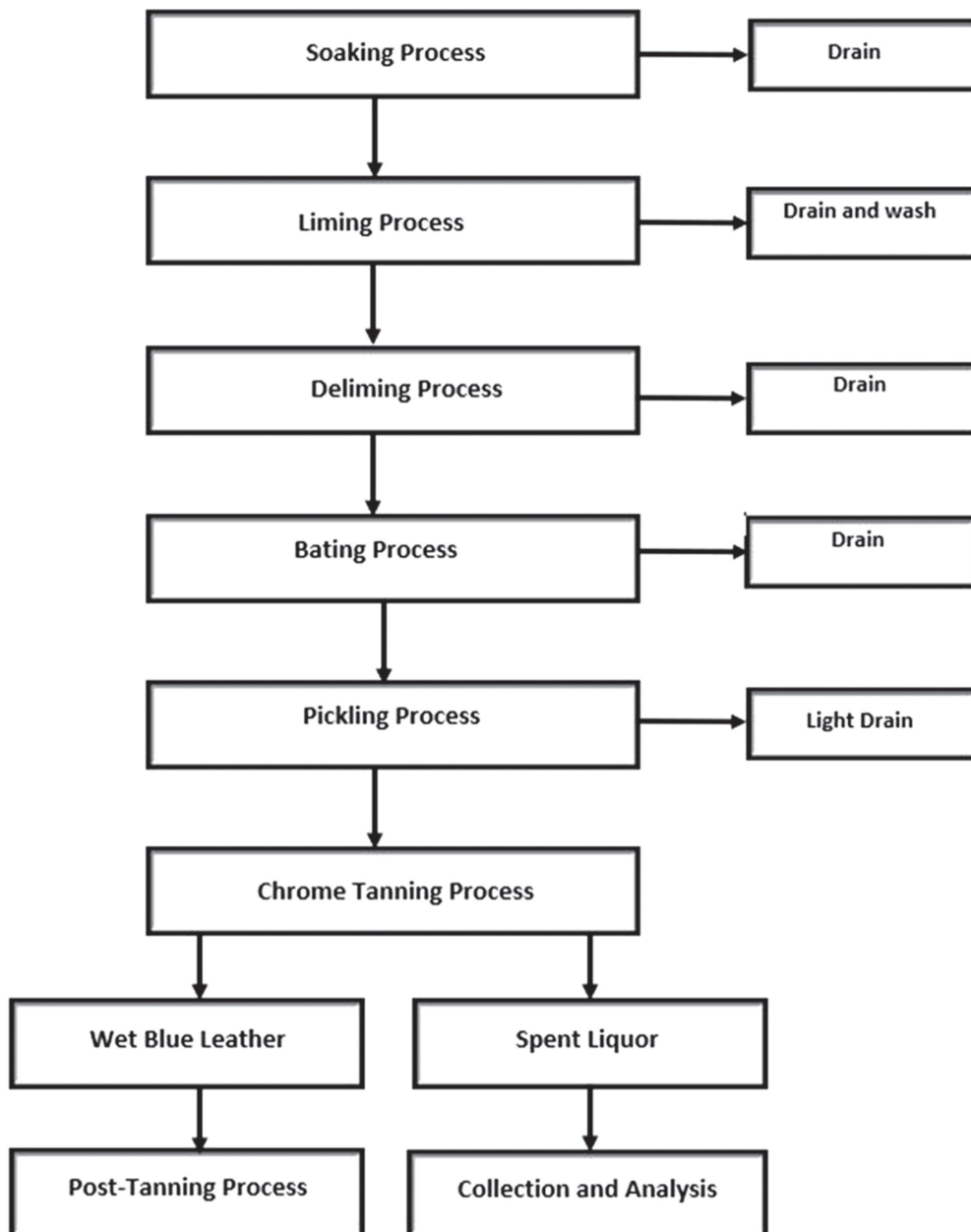


Figure 1. Collection of spent chrome liquor for analysis

Chemicals and apparatus

The chemicals used in this study, such as sodium-bicarbonate (NaHCO₃), magnesium oxide (MgO), calcium carbonate (CaCO₃), nitric acid (HNO₃), perchloric acid (HClO₄) and sulfuric acid (H₂SO₄), were of analytical grade and purchased from Sigma Aldrich, a German chemical company.

Measuring cylinders were used for measuring different volumes of chrome tan wastewater, supernatant, acid reagents and standard solutions. The dilution of the sample solution was performed using volumetric flasks.

Experiments and analytical methods

Chrome tan wastewater characterisation

The chrome tan wastewater was characterised for total chromium content (Cr), the pH, total dissolved solids, turbidity and conductivity by using the standard procedure [36]. The pH was measured with the pH meter. TDS, turbidity and conductivity were measured by using the HACH model of the digital reading-meter machine according to HACH instructions.

Removal of chromium through precipitation

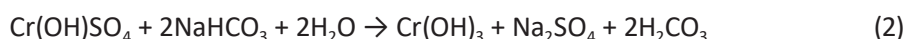
During this analysis, 250 ml of the sample (wastewater) was taken into 500 ml volumetric flask after screening through 2 mm sieve; then, arbitrary amounts of the considering precipitating agents (CaCO₃, NaHCO₃ and MgO) were used for the treatment of the effluent. These amounts refer to 0.25 gm/250 ml (1000 mg/L), 0.50 gm/250 ml (2000 mg/L) and 1 g/250 mL (4000 mg/L) doses respectively. The initial pH of CaCO₃, NaHCO₃ and MgO was 8.3, 9.91 and 9.0 respectively. The precipitating agents were added to each sample separately. The samples were then mixed for 1 hour at 150 rpm using a magnetic stirring machine. After 12 hours, the treated water (purified) i.e. supernatant solution was collected by filtration with Whatman filter paper no. 42, which was then followed by 30 minutes of settling of the precipitating agent. This supernatant solution was stored in the refrigerator at 4°C before the analysis.

The chemical reaction equations for all the three alkalis are as follows:

For CaCO₃:



For NaHCO₃:



For MgO:



The removal efficiency at different pH values was calculated as shown in Equation 4.

$$\% \text{ of Cr removal} = \left(\frac{C_i - C_f}{C_i} \right) \quad (4)$$

where C_i is the initial concentration and C_f is the final or supernatant concentration.

Determination of chromium concentration in the effluent and supernatant

Chromium(III) concentration of chrome tan wastewater, before and after the treatment, were measured by the atomic absorption spectroscopy (AAS) (Model: Perkin-Elmer model A analyst 200 Illinois USA) followed by the wet digestion method described by Javed et al., 2009 [37]. According to this method, a sample of 5 ml of water was taken into a 100 ml digestion vessel containing 10 ml of concentrated nitric acid and heated for 20 minutes. Sample was then cooled to room temperature. The content was then further heated vigorously after adding 5 ml of perchloric acid until the white fumes appeared and the sample volume reduced to 2–3 ml. The final volume was made to 50 ml by adding deionized water. Chromium concentration (a proper dilution of the sample to make the concentration limit at range) was then measured by AAS method at 357 nm wavelength, range of 0.1 to 15 µg/l (7 intermediate data) with an average of 5 duplicate sample analysis (the calibration curve is shown in Figure 3).

Recovery of basic chromium sulfate

For the recovery of Cr(III), the sludge or the precipitate was first heated at 700°C for 2 hours in a muffle furnace for the calcination of the protein part (present in the hide and the skin) and then mixed with H₂SO₄ in a stoichiometric ratio of 1:3 (the reaction was shown in equation 5). H₂SO₄ was added into the precipitating sludge dropwise, and after the addition was complete, the mixture was mixed for 30 minutes. This mixture was then filtered with Whatman filter paper no. 42.



The recovered chromium sulfate solution was evaporated in sunlight and the dry sludge i.e. chromium sulfate was obtained.

Digestion method for the solid sludge for chromium determination

A known amount of the sludge was digested in order to measure the concentration of the recovered Cr. By following the USEPA method 3050B [38], the recovered chromium sulfate was digested by acid. Around 300 mg of the dried recovered chromium sulfate was placed in a 50 mL beaker. 5 mL of 8 M HNO₃ solution was added to the beaker; a watch glass was used to cover the beaker and the unit was heated to 95°C in a hot plate. Concentrated HNO₃ (70%) and heating were successively added until no reaction with the sludge was noticed. The sludge was then digested for two hours at 95°C. After cooling, 1.5 mL of 30% H₂O₂ was added to the sludge and the temperature was increased to 95°C. H₂O₂ was added successively and heating was performed until no further reaction was noted. The sludge was then digested for 2 hours at 95°C. After cooling, the solution was filtered through a Whatman filter paper no. 1. 0.05 mL of the filtrate was diluted to a final volume of 50 mL with deionized water for Cr analysis. By atomic absorption spectrometry, the concentration of chromium was determined.

All the experiments were conducted in duplicate and results are presented as average of two.

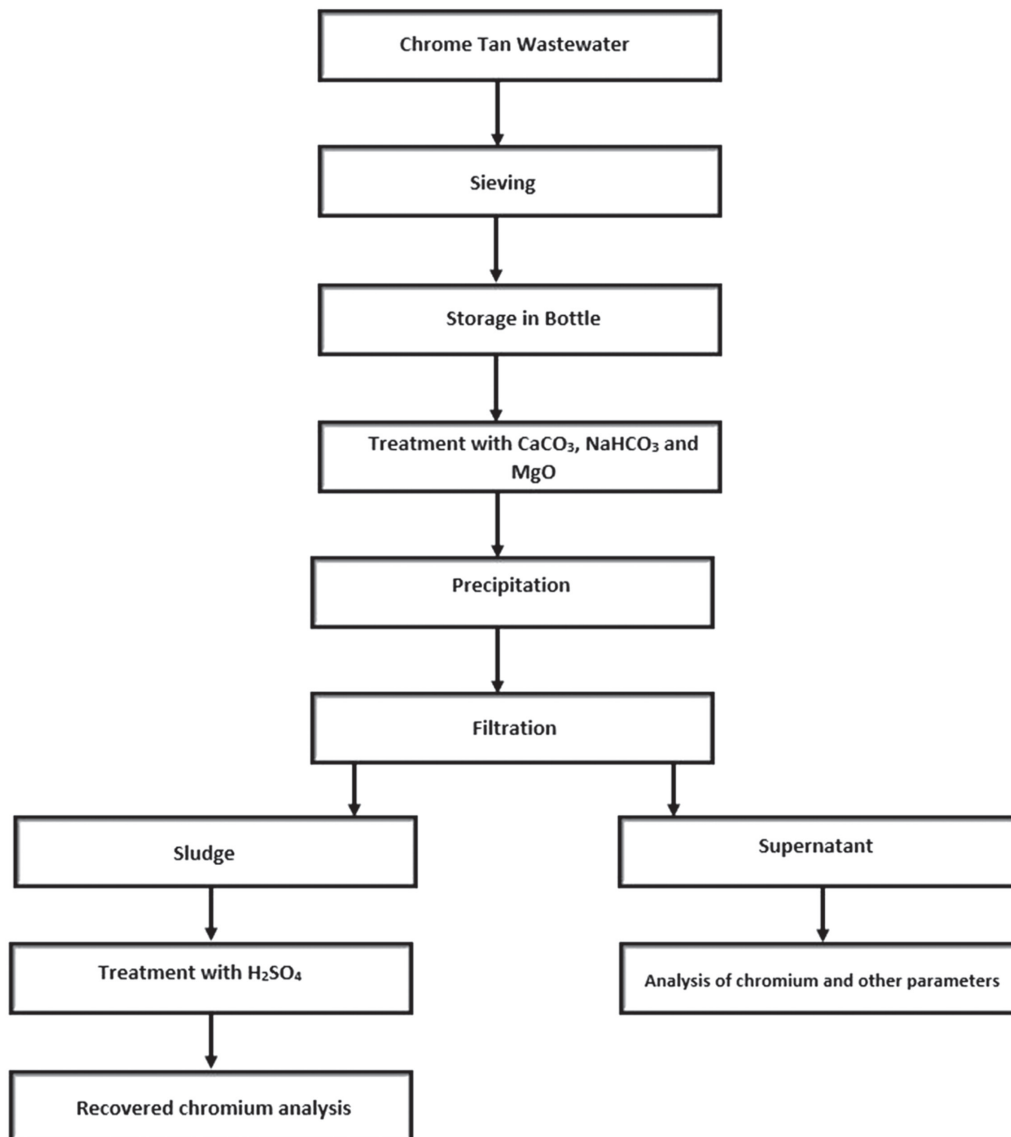


Figure 2. Removal and recovery of chromium with reduction of other physical parameters

RESULTS AND DISCUSSION

Chrome tan wastewater characteristics

The physicochemical characteristic of effluents is shown in Table 1, which indicates highly contaminated wastewater collected from the tannery. It was observed that the chrome tan wastewater had higher amounts of pollutants e.g. total dissolved solids (TDS) of 57150 mg/L, high chromium content (1002 mg/L), high conductivity (114500 $\mu\text{S}/\text{cm}$) and high turbidity (1050 NTU). Moreover, the pH was 3.1, indicating its strong acidic condition. All of these parameters confirm that this water, if disposed of in an aquatic environment without proper treatment, will pose a serious threat for the nearby environment (water bodies as well as human and plant life) [39]. Therefore, it is obvious that necessary measures should be taken to purify the chrome tan wastewater before it is discharged into the environment.

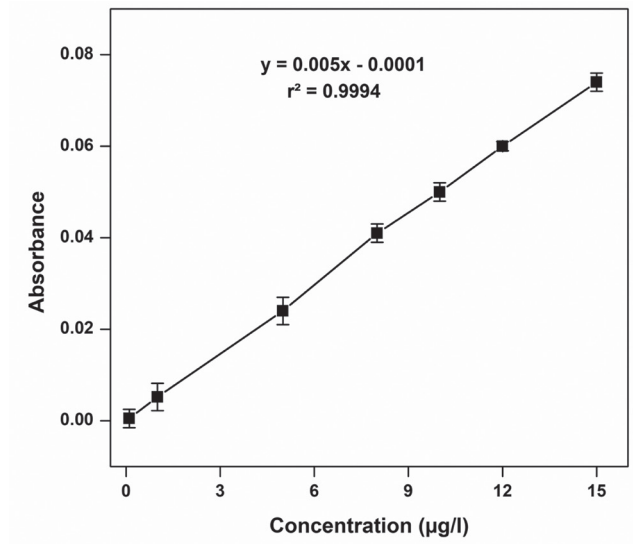


Figure 3. Calibration curve of chromium from 0.1 to 15 µg/l concentration.

Table 1. Physicochemical parameters of the tannery effluent

Parameter	Results
pH	3.1
Cr Concentration	1002 mg/L
TDS	57150 mg/L
Conductivity	114500 µS/cm
Turbidity	1050 NTU

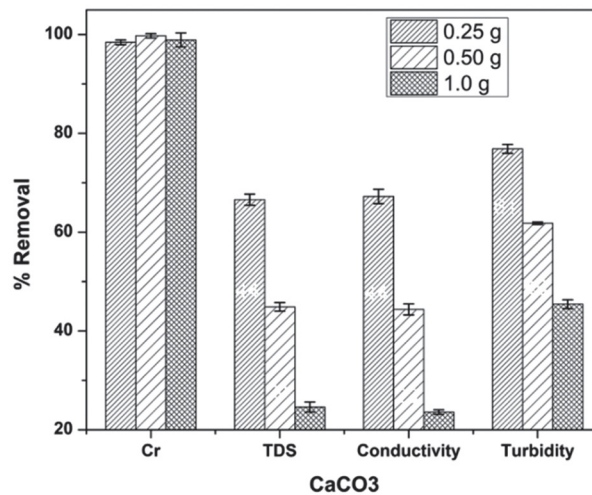


Figure 4. Percentage removal of physicochemical parameters via CaCO3 at 0.25gm/250ml (1000mg/L), 0.50gm/250ml (2000mg/L) and 1g/250mL (4000mg/L) dose.

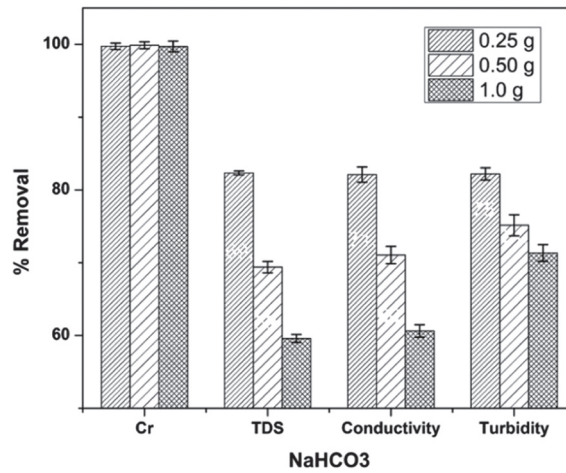


Figure 5. Percentage removal of physicochemical parameters via NaHCO₃ at 0.25gm/250ml (1000mg/L), 0.50gm/250ml (2000mg/L) and 1g/250mL (4000mg/L) dose.

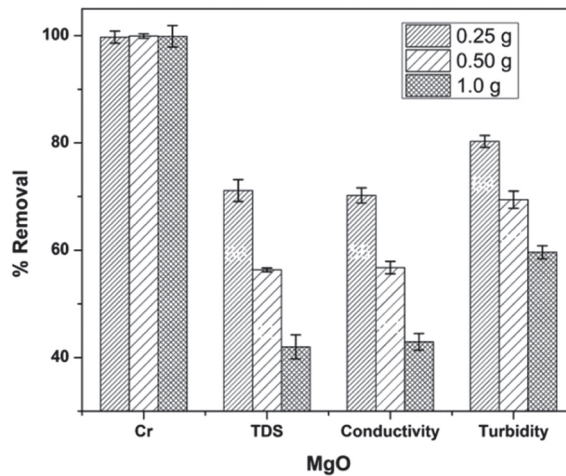


Figure 6. Percentage removal of physicochemical parameters via MgO at 0.25gm/250ml (1000mg/L), 0.50gm/250ml (2000mg/L) and 1g/250mL (4000mg/L) dose.

Comparative effect of pH on chromium removal while using the precipitating agents

The pH plays an important role in the removal of chromium by chemical precipitation technique. If the liquor pH is kept in between 5.5 to 12, the produced Cr(OH)₃ will not be dissolved [40].

The pH increases with the increase of doses of each precipitating agent. For CaCO₃, pH was found to be 7.4, 8.9 and 10.6 for 0.25gm/250ml (1000mg/L), 0.50gm/250ml (2000mg/L) and 1g/250mL (4000mg/L) dose respectively. For NaHCO₃, the highest pH (9.87) was found for the 4000mg/L dose and the lowest pH (7.2) was found for the 1000mg/L dose. A similar effect of the dosage on pH was found for MgO as well. In the case of MgO, for 1000 mg/L, 2000 mg/L and 4000 mg/L dose the pH was 7.81, 8.91 and 10.97 respectively. After adding each dose of the precipitating agents into beakers containing chrome tan wastewater solution, the pH value was noted (Table 2). The initial pH was found to be 7.2 after adding 0.25 g of NaHCO₃ to a 250mL solution. The pH increased with the increased amount of NaHCO₃. In the case of NaHCO₃ basic solution, the highest removal percentage of chromium (99.97%) was found at pH 8.31 and the lowest value (99.70%) was obtained at pH 9.87. The optimum pH value for Cr removal when using NaHCO₃ was observed at 8.31 according to the result of the experiment (Table 2). The chromium concentration in the supernatant was 0.3 mg/L, which is far below than the permissible (EEPA) limit (2 mg/L) (Figure 7).

Table 2. The efficiency of NaHCO₃ for Cr(III) precipitation at different pH values

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L)	Removal (%)
7.2	1002.6	0.78	99.92
8.31	1002.6	0.3	99.97
9.87	1002.6	2.94	99.70

Table 3. The efficiency of CaCO₃ for Cr(III) precipitation at different pH values

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L)	Removal (%)
7.4	1002.6	5.72	99.42
8.9	1002.6	0.5	99.95
10.6	1002.6	1.86	99.81

In the case of CaCO₃, maximum chromium removal efficiency (99.95%) was found at pH 8.9 and the minimum removal was observed at pH 7.4 (Table 3). This is because chrome precipitation is low at lower pH. There is an increase in removal efficiency with the increase of pH, however only after a certain limit; much higher pH causes re-dissolution of chromium into the solution. The chromium concentration was 5.72 mg/L at pH 7.4 and 0.5 mg/L at pH 8.9 (Figure 7). However, at pH 10.6 chrome concentration was 1.86 mg/L. This may be because of re-dissolution of chromium at higher pH. The optimum pH value was 8.9 (Table 3).

Table 4. The efficiency of MgO for Cr(III) precipitation at different pH values

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L)	Removal (%)
7.81	1002.6	1.12	99.89
8.91	1002.6	0.2	99.98
10.91	1002.6	1.25	99.88

From the Table 4, in the case of MgO, the maximum chromium removal was observed at pH 8.91 and minimum was at pH 10.91. The optimum pH value was 8.91. In the case of MgO, the chrome concentration was below the EEPA permissible limit (2 mg/L) at all the resulting pH values (Figure 7). The findings are quite similar to the results reported by Esmaeili et al., 2005, in which the optimum pH was between 8 and 9 [3].

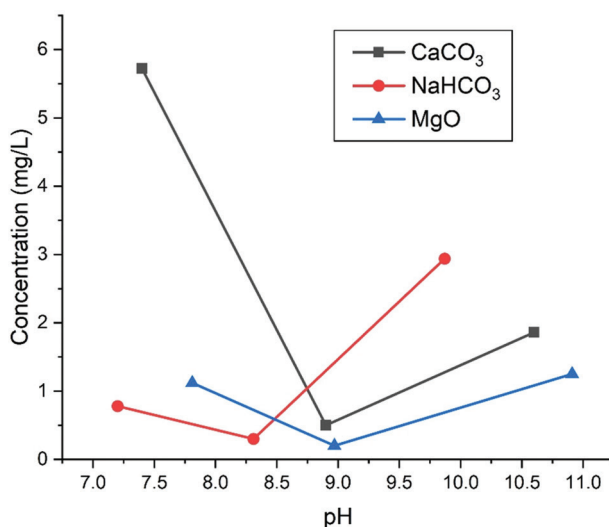


Figure 7. Chromium concentration in the supernatant solution vs pH for the three precipitating agents

Chromium concentration is high since the reactivity and solubility of MgO is low at lower pH values. The optimum conditions for the three precipitating agents are compared as indicated in Table 5. While comparing the removal efficiency for the three precipitating agents, MgO showed maximum percentage of chromium removal efficiency at pH 8.91 (99.98%) and it is the highest and the best of all three.

Table 5. Chromium removal efficiency at optimum pH for the three precipitating agents

Precipitating agent	Optimum pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L)	Max. % of Cr removal
CaCO ₃	8.9	1002.6	0.5	99.95
NaHCO ₃	8.31	1002.6	0.3	99.97
MgO	8.91	1002.6	0.2	99.98

Removal of chromium and other physicochemical parameters from effluents

Removal percentage of chromium and other physical parameters by several precipitating agents was shown in Figures 4, 5 and 6. This indicates that all of the precipitation agents have almost the same ability to remove Cr(III) from effluents (almost 97-99 %), and also that changing the dose slightly changes the recovery results (though 0.50 g shows the best result).

When chrome-tanning effluent was treated with MgO, it gave a compact, grainy, dense sludge that easily settles. This may be partly explained by Lippmann’s theory [41], which claims that the basicity of the MgO surface is strong enough to precipitate many of the heavy and hazardous metals encountered in chrome tan wastewater streams [42]. This has been shown in Table 6. Besides, the metal precipitates are negatively charged, therefore they cement to the MgO surface to give a compact sludge and denser residues [43], whereas the sludge formed by NaHCO₃ and CaCO₃ is gelatinous. This is in agreement with the report of Esmaeili et al. (2005) [3]. And when NaHCO₃ is employed, the neutralization reaction occurs at a homogeneous phase.

On the other hand, with the increase of the dosage of each precipitating agent, removal percentages of TDS, conductivity and turbidity were significantly reduced which is due to the addition of a large quantity of the precipitating agent, which itself produces cation and anion and the resulting large ionic particles. Table 6 shows overall TDS, conductivity and turbidity value. In the case all of the precipitating agents it was also shown that increasing the dose to 1 g/250 mL leads to a reduction in Cr removal. This may be due to re-dissolution of Cr from the precipitating surface, or it may be due to the possible aggregation of the precipitating agent in the settling period which reduces the surface area for Cr(III). In this study, NaHCO₃ shows better performance among other precipitating agents in terms of removal of all parameters. A 1000 mg/L dose of NaHCO₃ approximately reduces 99.72, 82.33, 82.10 and 82.19 % of Cr, TDS, conductivity and turbidity respectively (Table 6). Similarly, MgO and CaCO₃ also showed significant reduction of TDS, conductivity and turbidity even at a low dose.

Table 6. Other parameters removal efficiency of the precipitating agents

Dose	0.25g/250 mL			0.50g/250 mL			1.0g/250 mL		
	Conductivity removal (%)	TDS removal (%)	Turbidity removal (%)	Conductivity removal (%)	TDS removal (%)	Turbidity removal (%)	Conductivity removal (%)	TDS removal (%)	Turbidity removal (%)
CaCO ₃	67.24	66.58	76.86	44.37	44.88	61.81	23.58	24.58	45.43
NaHCO ₃	82.10	82.32	82.19	71.05	69.38	75.14	60.61	59.58	71.33
MgO	70.22	71.13	80.28	56.77	56.34	69.43	42.92	41.99	59.62

Table 7. Chromium recovery efficiency of the three precipitating agents from the precipitating sludge

Dose	0.25g/250 mL	0.50g/250 mL	1.0 g/250 mL
Precipitating agent	Chromium concentration after recovery (mg/l)	Chromium concentration after recovery (mg/l)	Chromium concentration after recovery (mg/l)
NaHCO ₃	881.3	880.4	874.4
MgO	921.2	908.4	912.7
CaCO ₃	879.2	891.6	874.2

Recovery of chromium from the precipitating sludge

According to the title of the study, only the recovery of chromium from the precipitating sludge has been shown. After the removal, the chromium concentration in supernatant was so low that the amount was a lot below the permissible limit. There was not much benefit to recovering chromium as the concentration of chromium was found very low in supernatant and it can be discharged into the environment. After the removal, the supernatant was discharged into the environment. Only the precipitating sludge was recovered and the concentration of the recovered chromium in the sludge has been shown in Table 7. The recovery amount will vary if the recovery method varies.

The recovery of chromium does not follow the pattern like the removal of chromium, considering the chromium concentration in the supernatant, shown in the Table 7. Table 7 shows that, in the case of NaHCO₃, increasing the dose of the precipitating agent decreases the recovered Cr concentration. However, in the case of MgO, the concentration decreases with the decrease in the dose and vice versa, whereas for CaCO₃, the pattern is quite opposite to that of MgO. All three precipitating agents showed different patterns of change in the recovered Cr concentration. Among these precipitating agents, MgO showed the maximum concentration of the recovered chromium. This might be due to the tendency for the interfacial energy between the liquid phase and the particles of MgO, which plays a dominant role. The maximum concentration of the recovered chromium was found to be 921.2 mg/ L when using MgO.

It is likely that the recovered chromium in the sludge is lower than the initial chrome concentration. This is a usual fact as low chrome recovery often occurs due to the incomplete dissolution of the sludge in acids [43]. The leaching of chromium depends on various factors like the type of the acid used, the temperature, the extraction time etc. [44]. The study focuses on a particular recovery method to show the comparative effects of the three precipitating agents on the recovery of chromium from the sludge.

In this study, Cr(III) was recovered from the sludge by treating the sludge with H₂SO₄. J. Kanagaraj et al. (2008) used the recovered chromium used in chrome tanning from the precipitate, used it to produce leather, and tested the physical properties of the produced leather [45]. Minas et al. utilized the recovered sludge for the production of a chrome-tanning agent that would be re-used in chrome tanning [46].

This recovered chromium has a lot of potential to be used in tanning and some of the post-tanning operations.

CONCLUSION

This research has explored the potential of using NaHCO₃ and CaCO₃ in comparison with MgO, as precipitating agents for the removal and the recovery of chromium from chrome tan wastewater. The removal efficiency of TDS, conductivity and turbidity were also analysed since these are important physicochemical parameters of the effluent. For NaHCO₃ and CaCO₃, the maximum removal efficiency (99.97% and 99.95% respectively) of chromium was found at pH 8.31 and 8.9, whereas MgO showed the highest efficiency

(99.98%) at pH 8.91. The highest efficiency of all the three precipitating agents was observed at a dosage of 0.5 g/250 mL (2000 mg/L) for the removal of chromium from chrome tan wastewater. In the case of NaHCO₃, the maximum redissolution of chromium(III) was observed at pH 9.87, whereas MgO showed the lowest redissolution of chromium(III) out of the three, even at pH 10.91. The lowest chromium concentration in the supernatant was found to be 0.3 mg/L, 0.5 mg/L, and 0.2 mg/L for NaHCO₃, CaCO₃ and MgO respectively at the dosage of 0.5 g/250 mL (2000 mg/L). However, in the removal of other physical parameters, NaHCO₃ showed great performance, even better than MgO. The removal percentages for conductivity, TDS and turbidity were found to be 82.10 %, 82.32 %, 82.19 % respectively. The maximum concentration of the recovered chromium from the precipitating sludge for MgO was found to be 921.2 mg/L at the 0.25 g/250 mL dose, whereas NaHCO₃ showed 881.3 mg/L and CaCO₃ showed 891.6 mg/L as the highest concentration of the recovered chromium at the doses of 1000 mg/L and 2000 mg/L respectively. This study suggests that these precipitating agents can be used for the treatment of the tannery effluent. Though MgO showed the highest performance in the removal and the recovery of chromium, the results of other precipitation methods using NaHCO₃ and CaCO₃ as precipitating agents were satisfactory. NaHCO₃, CaCO₃ and MgO are highly available at a lower cost compared to other precipitating agents. Moreover, the recovered chromium from the precipitating sludge can be re-used in chrome tanning rather than be discharged into the environment. Thus, the environmental impact of chromium can be minimized.

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