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A lab-scale study for efficient removal of Cr from leather industry wastewater

Aqsa Riaz, Sofia Nosheen*, Tahira Aziz Mughal, Saira Riaz

Department of Environmental Science, Lahore College for Women University, Lahore, Pakistan

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Abstract

The leather tanning industry is the second most dynamic industry in Pakistan. It generates all sort of wastes including a large number of effluents which remains untreated causing adverse environmental impacts. In the present study, the practical focus is given to find the best innovative and low-cost approach for the treatment of Chromium in the wastewater. It highlighted coagulation using MgO, adsorption using activated carbon, and biosorption using bark and leaf extracts of *F. religiosa* (peepal tree). Among various applied approaches activated carbon gave the best results in terms of removal efficiency (above 90 %) even at higher Cr concentration (100 ppm) while bark extract of *F. religiosa* also showed 80% removal efficiency (25 ppm Cr concentration). Furthermore, it was revealed that greater than 90% removal can be achieved with just 5 mg of adsorbent dosage. Contact time showed an enhanced positive effect on the removal of toxic metal Cr. at 60 min shaking. An overall study proved that activated carbon is a good adsorbent for removal of Cr from wastewaters and green bio sorbents can also be used as a sustainable low-cost effective treatment for leather industry wastewater.

* **Corresponding Author:** Sofia Nosheen ✉ nosheen.sofia@yahoo.com

Introduction

Tanning is an important process for transforming raw hides into several leather goods, which are used daily by the consumers (Lofrano *et al.*, 2013). Today chromium salts (around 33% basic chromium sulphate) are extensively used as a tanning material. The hides and skins tanned with Cr salts have a better mechanical property, remarkable dyeing propriety and hydrothermal property in comparison with hides and skins which are interacted with other tanning materials. The leather takes up around 60% of applied chromium and the rest of the metallic salts (40%) are usually discharged into wastewaters during the tanning period which has serious environmental impact (Chowdhury *et al.*, 2013).

In Pakistan, the leather tanning industry is considered to be one of the main industrial sectors. The Government of Pakistan in 2011 rated the leather industry sector to be the second most dynamic industrial sector after the textile sector. The leather sector contributes 5 % to manufacturing GDP and about 7 % of the earning comes from it and it has provided employment to more than 200,000 workers in Pakistan (Badar *et al.*, 2016). The leather sector can be further categorized into six sub-sectors which are leather footwear, tanning, leather gloves, leather garments, leather goods and leather shoe uppers. The leather process industry is mainly present in Karachi, Lahore, Sialkot and Kasur. There are more than 2500 tanneries present in these cities (GOP 2011). Leather tanneries in Pakistan produce all three categories of waste: wastewater, solid waste and air emissions. However, wastewater is by far the most important environmental challenge being faced by Pakistan's tanneries. Although the exact quantity varies widely between tanneries, a normal requirement of around 50-60 liters of water per kilogram of the hide is suggested. Tannery wastewater is highly polluted in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, settleable solids, total kjeldhal nitrogen, conductivity, sulphate, sulphide and chromium. The values of these parameters are very high as compared to the values mentioned in the National Environmental Quality Standards (NEQS) set by the Government of Pakistan (Mehmood, 2008).

Several pieces of research on tannery effluent treatment using different technologies such as floatation, electrochemical treatment, sedimentation, coagulation, filtration, ultrafiltration and reverse osmosis process have been reported (Naumczyk and Rusiniak, 2006; Ates *et al.*, 1997; Song *et al.*, 2004; Krishnomoorthi *et al.*, 2009). Coagulation or chemical precipitation has been known for wastewater treatment since the previous century in England where lime was used as coagulant alone and/or in combination with calcium chloride or magnesium (Genovese and Gonzalez, 1998).

Leather tanning industries have adverse health impacts on human beings. According to the Occupational Safety and Health Administration, chromium which is one of the major pollutants of leather tanning industries can cause lung cancer; irritation or damage in the nose, throat, and respiratory tract due to breathing in a chromium-polluted environment; and skin and eye rashes can also be caused due to the direct contact of chromium (OSHA, 2006). If it comes in contact with the skin, the consequences are harmful such as skin damage or critical burns. It may even disturb the healing process of scrapes and cuts (Melissa, 2002). The effluent from tanning industries is considered to be difficult because of the presence of many chemicals that have low biodegradability and hence it poses a great concern to the environment. As a result, several researchers have worked on the treatment of tannery effluents using different technologies (Buljan and Kral, 2011).

So, there is an urgent need for a sustainable solution to wastewater generated from leather tanning industries. This present project is designed by keeping to find a low-cost, effective and eco-friendly solution to the above-said problem. In this study, different wastewater treatment techniques were compared so that the best technique could be figured out.

Methodology

A lab-scale set of experiments for the removal of Cr were performed using 25 to 100 ppm of solutions prepared from potassium dichromate as a source.

The treatment methods used for the study were coagulation using MgO, Adsorption using activated charcoal and biosorption using aqueous extract of *F. religiosa* bark and leaf.

The bark and leaf of *F. religiosa* were collected from a residential area of Lahore. These were washed thoroughly to remove any dirt and then oven-dried for 3 hours. The bark and leaves were grounded in a grinder and sieve to get a fine powder which was stored separately in airtight containers. The extracts of bark and leaf were prepared in water which is a universal environment-friendly solvent by boiling in 1:20 (w/v). After filtration, the residue was discarded while the filtrate was stored at 4°C for further use.

Batch study

A batch scale set of experiments were conducted. The initial and final concentration of chromium in every set of experiments was checked by Atomic Absorption Spectroscopy (Thermo Scientific; Solaar software).

The number of chromium ions adsorbed was calculated using the following formula:

% Adsorption = $(C_i - C_f) / C_i \times 100$

Where C_i is the initial concentration and C_f is the final concentration of Cr (Argun *et al.*,, 2006).

Three experimental conditions were optimized i.e. contact time (40, 60 min), dosage (1, 5 mg) and concentration of targeted metal ions (25-100 ppm) which is to be removed. 25 ml of aqueous Cr solution was used for each concentration for the treatment application.

Results and discussion

Effect of dosage

The optimization of adsorption dosage is one of the most fundamental parameters for the treatment of wastewater by adsorption.

When using the optimized adsorbent dose, not only is the adsorption effect maximized but also the amount of adsorbent is fully utilized. Therefore, it is extremely important to optimize the dose of adsorbents.

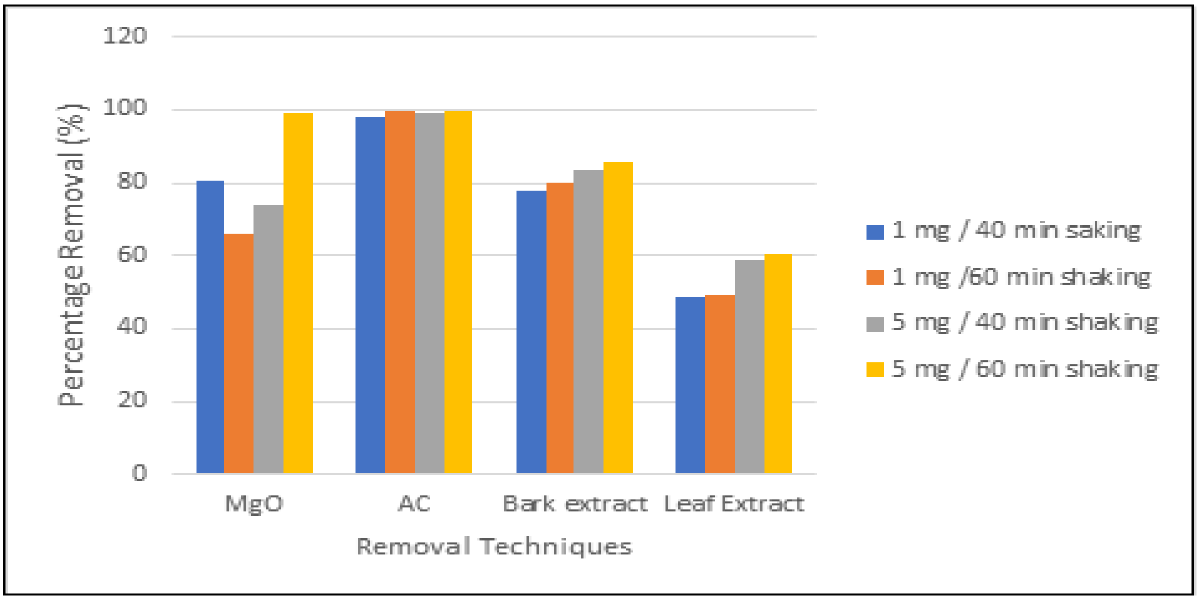

Fig. 1. The percentage removal of Cr. (25 ppm) with various sorption options.

In the present study, optimization of adsorbent dosage was evaluated using 1 and 5 mg of Activated carbon and MgO whereas 1-ml and 5-ml aqueous bark and leaf extracts of *F. religiosa*. It is seen from the results (Fig. 1-4) that adsorption efficiency of activated carbon was maximum (89-99 %) as compared to the other treatment techniques and remained nearly constant for all experimental conditions even at higher Cr concentrations. This shows that activated carbon can give higher efficiencies for Cr removal even at low dosages which is due to the greater availability of adsorption sites of activated carbon and thus making easier access for Cr to adsorption sites (Mohan *et al.*, 2006).

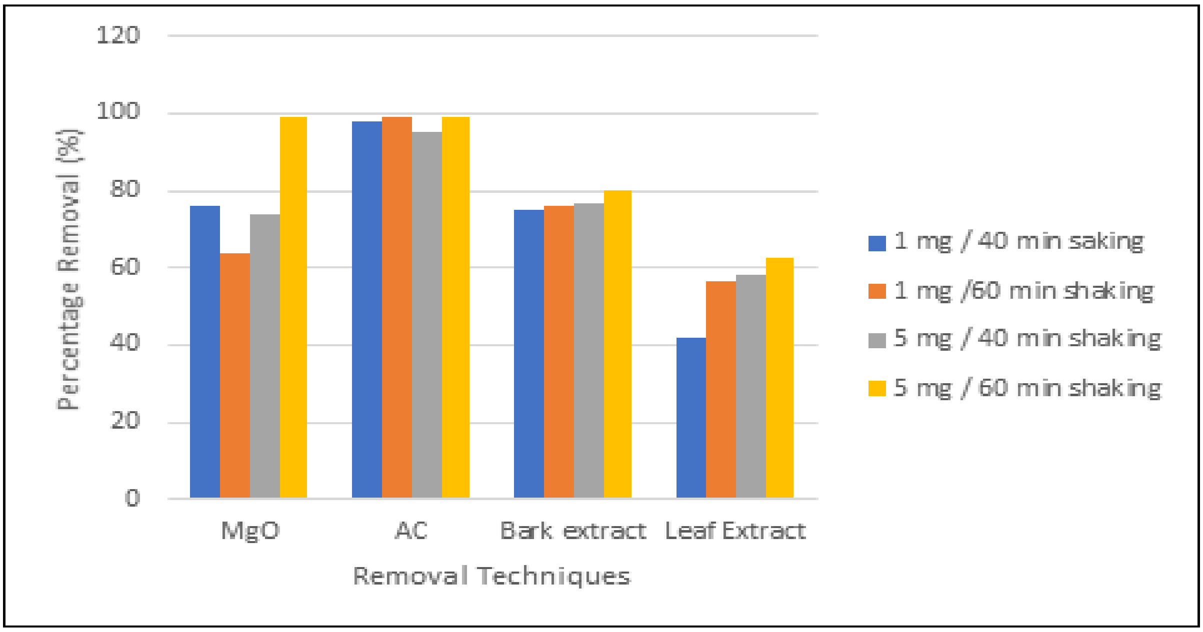

Fig. 2. The percentage removal of Cr. (50 ppm) with various sorption options.

Activated carbon is a good adsorbent for chromium removal because it has a well-developed porous structure and a high internal surface area for adsorption (Anirudhan and Sreekumari, 2011). Whereas, an increasing trend of removal efficiency was seen with MgO when the dosage was increased. At low dosage (1 mg/L) MgO showed 80.6 % of Cr removal which increased to 99 % when the dosage was increased to 5 mg/L. At low dosage (1 mg/L) there are fewer precipitants to form precipitates but when the dosage increases the removal efficiency also increases as more precipitates are formed. Cr when comes in contact with MgO forms a complex "$MgCrO_4$" which is insoluble in aqueous medium and easily precipitates in solutions (Fran and Mooney, 2006). The same trend can be seen for all Cr concentrations (25-100 ppm) as seen in Fig. 1 to 4.

Biosorption study of bark and leaf extracts of F. *religiosa,* also showed an increase in removal efficiency with the increase in extract dose. Comparatively bark extract showed better results with a removal efficiency of 85.7 % (5 ml dose) as compared to leaf extract which showed removal of 60.68 % (5ml dose) at 25 ppm Cr concentration. It has been reported that the biosorption percentage of modified bark extract of *Moringa* is comparatively higher and thus efficient than the biosorption percentage of modified leaf extract (Shinomol *et al.*, 2016). Bark extract is considered to be a tannin-rich part of *F. religiosa*. The positively charged heavy metal ions come in contact with the weak acids of tanning agents and forms precipitates and this is how the Cr is removed from the aqueous solutions using plant extracts (Lucaci *et al.*, 2011; Kokorevics *et al.*, 1999; Sen *et al.*, 2012; El-Latif and Ibrahim 2009; Semeykon and Tikhomirova 2015.

Effect of contact time

Contact time is another significant parameter for the removal of heavy metals. Adsorption property is extremely dependent on contact time between the adsorbent material and the adsorbate. It is seen from Fig. 1 to 4 that activated carbon showed almost constant removal results at all contact times (40 min and 60 min shaking) and gave removal efficiency of above 89% for all the optimized conditions at all concentrations. MgO on the other hand showed a decreasing trend in Cr removal with an increase in contact time at low dosage (1 mg/L) whereas, an increase in removal efficiency was seen with the increase in contact time when the dosage was increased (5 mg/L), so the optimum time for Cr removal at low dosage was 40 min after which removal efficiency decreases since all the precipitates are formed but with a higher dose, the pH increases and at higher pH values the precipitation also increases. The same trend was seen for all Cr concentrations (25-100 ppm).

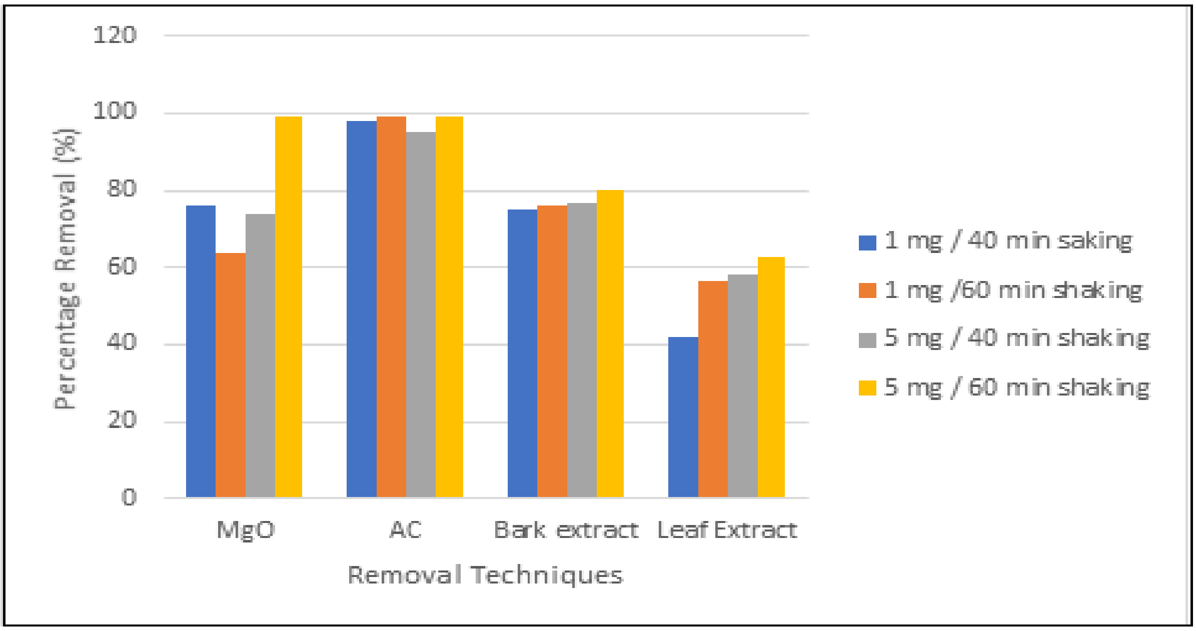

Fig. 3. The percentage removal of Cr. (75 ppm) with various sorption options.

Biosorption with bark and leaf extracts of *F. religiosa* showed the optimum contact time to be 60 min at which maximum removal efficiency was achieved. The increase in contact time gives more time for the tannins to form a complex with the metal ions and therefore better removal efficiency was achieved.

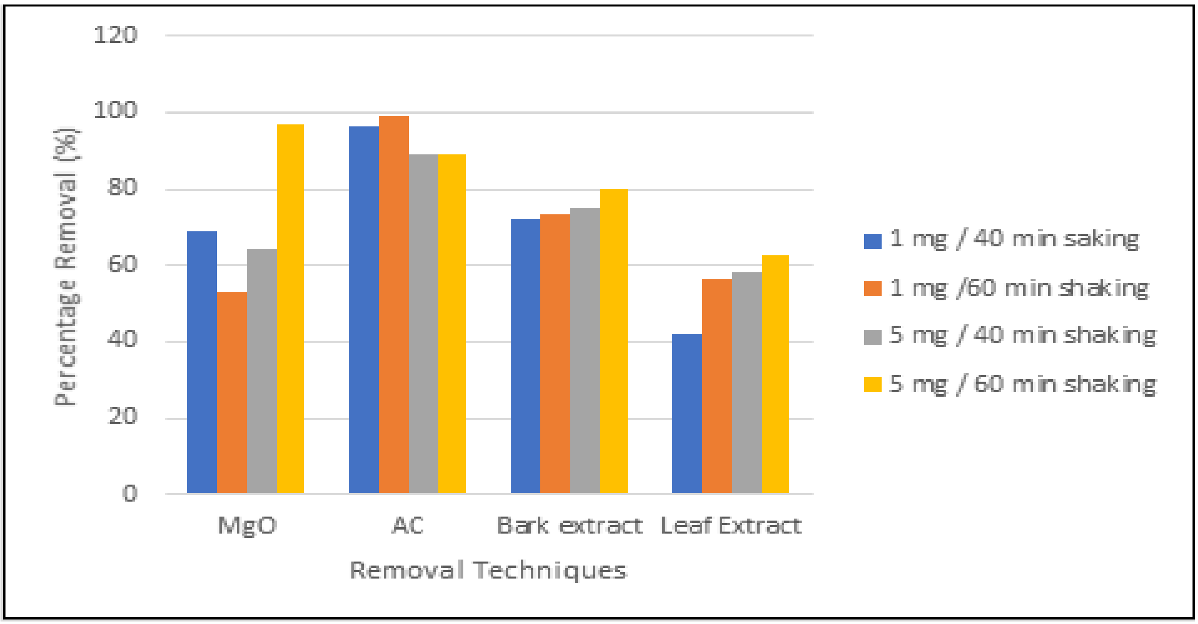

Fig. 4. The percentage removal of Cr. (100 ppm) with various sorption options.

Effect of concentration

A decrease in removal efficiency was seen with the increase in the concentration of Cr in the case of sorption with MgO, activated carbon and bark extract of *F. religiosa*. It is explained that at low concentrations, there are specific sites where the metals are adsorbed and when concentration is increased, those sites are saturated and the exchange sites are filled leading to less adsorption efficiency (El-Ashtourkhy *et al.*, 2008). Whereas the leaf extract of *F. religiosa* showed an increase in removal efficiency with the increase in the concentration of Cr but after the optimum removal was achieved, a decrease in removal was seen with an increase in Cr concentration. This is because, after a certain level of increase in Cr concentration, all the active sites for precipitation gets occupied and finally establish a form of dynamic equilibrium between the processes of adsorption and desorption (Malkoc *et al.*, 2006; Simha *et al.*, 2016,).

Conclusion

It is concluded from the results that the best results for Cr removal were achieved with 5mg dose of activated carbon and MgO whereas 5 ml extracts of bark and leaf extract of *F. religiosa* were the optimum dosage. Optimum contact time was 60 min shaking. Activated carbon is a good adsorbent for the removal of Cr. from wastewaters with a removal efficiency of 99% and biosorption with bark extract of *F. religiosa* can also be a good biosorption option for Cr. recovery as it can also give the removal of the above 80%.

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