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STUDIES ON RECOVERY OF CHROMIUM FROM TANNERY WASTEWATER BY REVERSE OSMOSIS

ALKA TRIPATHI AND ANJANI KUMAR DWIVEDI [#]

Department of Chemical Engineering, Ujjain Engineering College, Ujjain (M.P.), India

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ABSTRACT

Chromium (Cr) is the most important element used to leather industry is still considered to be the most important industries which pollute the environment by chromium metal. Removal of heavy metals dissolved at low concentrations in water and wastewaters is often a problem that can be solved in different ways. This paper describes a study conducted to determine the recovery of chromium from tannery wastewater by reverse osmosis. The effluent is first subjected to the gravity settling, followed by alum treatment. The supernatant is then treated with the subsequent reverse osmosis after a coarse filtration by a fine cloth. The coagulant is determined by adding 0.5 to 2.5 g/L alum to the effluent and measuring BOD, COD, TDS, TSS and pH, at the different dose of alum. Therefore, 1.5 g/L is considered as the optimum alum dose. Spiral wound module with thin film composite membrane is used in this experiment. Coagulated water is treated by RO at various pressures (100, 120 and 150 psi). The best treatment efficiency was obtained at 150 psi. Initial Cr concentration in feed waster is 14.2 mg/L. The Cr removal efficiency of treatment by RO is 98.66 % at pH range of5.6 to 7 and in temperature of about 25°C at an applied pressure of 150 psi. It could be concluded that RO membrane process may be selected and developed as an effective alternative for treatment of metal contaminated effluents of leather and similar industries.

INTRODUCTION

Increasing industrial density, human population, and use of the old and polluting technologies lead to increasing environmental pollution. Since the environmental protection has now become a global issue, a cleaner and greener technology is warranted for the abatement of the industrial pollution. In India, the annual amount of hides and skins processed is about 70,000 tones resulting in 75,000 m^3 of the liquid effluent per day (Purkait *et al.*2005) The leather industry is one such highly polluting industry. It is a natural product like wool and is obtained from a variety of animals, like, cows, sheep, goats, etc. Leather and leather goods industry is one of the biggest small scale industries in India and this industry is scattered unevenly in the country. The main centers of tanning industry in India are located in Westbangal, Tamil Nadu, Uttarpradesh, Maharashtra, Punjab

***Corresponding Author Email :** alka84.tripathi@gmail.com

Karnataka, Orissa, Andhrapradesh, Rajasthan, Madhyapradesh. State wise Himachal Pradesh and Punjab produce the maximum number of cattle skins West Bengal produces maximum buffalo skins, Kerala and Madras sheep skins while Uttar Pradesh Produces Goat skins (Kaul, 2005).

Chromium (Cr) is the most important element used to plate other metals and leather industry is still considered to be the most important industries which pollute the environment to this metal (Ameri *et al*. 2008). Chromium (Cr) is the first element in Group 6 B of the periodic table and belongs to the transition metals. It occurs in nature as the 21st abundant element and it has two valences of +3 and +6.Cr in its +6 valence form is very toxic and is considered as an undoubtful carcinogen. It is introduced to our environment through wastes discharged from many industries as well as from its natural sources namely many minerals and ores such as the ore chromite (WHO, UNEP 1988). The greatest content of chromium (III) is found in the tanning wastewater. The composition of this effluent varies according to the tanning process used and to the type of leather to be obtained. Most of the components of the tanning wastewater and their most frequent contents are: 16–25 g/L sulfate, 17-26 g/L chloride, 14-21 g/L sodium, 0.6-2.0 g/L of chromium (III) and a residual acidity between pH 3.5 and 5.0 (Harris,1996).

The tanning process is one of the largest polluters all over the world. Industrial wastewater have various materials can cause pollution Inorganic salts, Acids and Alkalis, organic matters, suspended solids, floating liquid and solid,colour, toxic chemicals, microorganism, radioactive materials, and foam producing matter etc. Characteristics of tannery wastewater general characteristics of tannery wastewater is complex composition, color depth, suspended solids and more high oxygen consumption, large fluctuations in water quality and quantity. Suspended solids (SS) for a lot of lime, broken skin, hair, oil, meat residue and so on (Kaul, 2005). The transformation of the raw hide into leather requires various mechanical treatments and also a series of chemical treatments. Chemical processing is generally carried out using different chemicals; e.g., acids, alkalis, salts of sodium and chromium, dyes, etc (Dutta, 1999).

The most important processes to remove the chromium (III) from the tanning wastewater are precipitation, adsorption, ion exchange, reverse osmosis etc. Cr removal can be much better accomplished by RO technology com-pared to many other processes (either chemical or biological) witch had been used for tannery or other industrial effluents treatment (Hintermeyer *et al.* 2008). This superiority may also be expected for treatment by RO in removing similar toxic heavy metals which are often present in industrial effluents and are not efficiently removed by conventional treatment(Eckenfelder, 2000) RO has been widely applied to separate or concentrate aqueous solutions containing organics or salts (Gholami, 2002). It involves separating water from a solution of dissolved solids by forcing water through a semi permeable membrane. As pressure is applied, larger molecules such as metal ions are retained by the membrane. The purified stream is called permeate and the concentrated stream is called concentrate (WEF, 2006). Membranes are usually assembled in modules, each of which compacts a membrane of large surface area within a cylindrical shell of small volume. The type of commercially available module is the spiral-wound and the membrane materials which are in common use are aromatic polyamide and cellulose acetate. The main advantage of membrane based process is that concentration and separation is achieved with on change of state and without using chemicals and thermal energy, the process energy efficient and ideally suitable for recovery applications (Badalo *et al.* 2005).

This paper describes a study conducted to determine the recovery of chromium from tanning wastewater by using reverse osmosis also determine the characteristics of tannery wastewater before and after RO treatment. However, conventional treatments such as those used for urban wastewater are not able to reduce the salt concentration sufficiently and new methods need to be studied in the light of new technologies. In this aspect, membrane technology is increasingly used as a separation technique in chemical and environmental engineering, including desalination, selective separation and wastewater treatment.

Method

Effluent is collected from the leather industry. The effluent was blackish color have large amount of BOD, COD, pH, TDS, TSS and chromium. For the measurement of BOD,COD, TDS, TSS, pH and Cr various chemicals used in the experiment such as sulfuric acid, potassium dichromate, silver sulfate, ferrous ammonium sulfate (FAS), ferroin indicator etc. Potassium alum is used for the coagulation and is procured from the local market. All chemicals

such as are of analytical grade and are used without further treatment.

The effluent is pretreated by screening to remove large floating and suspended solids which could interfere with the reverse osmosis operation. In the screening undesirable substance retained over the screen and liquor is passed to the screen. After the screening the effluent is sent to the coagulation.

In the coagulation the effluent is kept in five 500 mL capacity beakers. The optimum coagulant is determined by adding 0.5 to 2.5 g/L alum to the effluent and measuring BOD, COD, TDS, TSS and pH at different alum dose. Once the optimum coagulation dose is obtained, the supernatant of the gravity settled liquor is treated with the optimum alum dose. The gravity settlement is carried out in a 10 liter container. After coagulation, the sludge settles at the bottom and the supernatant is siphoned out. A fine nylon filter cloth is then used for further clarification of the collected supernatant. The clarified liquor is then treated reverse osmosis process. The clarified effluent is pumped by a high pressure reciprocating pump from the stainless steel feed tank to the cross flow cell with a rectangular channel. To obtain the best efficiency to remove Cr, the wastewater treated with RO at different pressures (100,120,150 psi).

Industrial RO use spiral wound membrane mounted in high pressure containers. The membrane stack is two, very long semi permeable membrane with spacer mesh between than that is sealed along the two long sides. This is then wound up in a spiral tube with another spacer to separate the outside of the stack. The spiral winding provides a very high surface area for transfer. Between each membrane layer is a mesh separator that allow the permeate (pure) water to flow. Water is force in one end of the spiral cylinder and out the out other end. Back pressure force the water through the membrane where it is collected in the space between the membranes. Permeate then flow around the spiral where it is collected in the center of the tube. Permeate samples are collected from the bottom of the cell and are analyzed Cr, COD, BOD and pH. The method used for hexavalent Cr determination was the standard

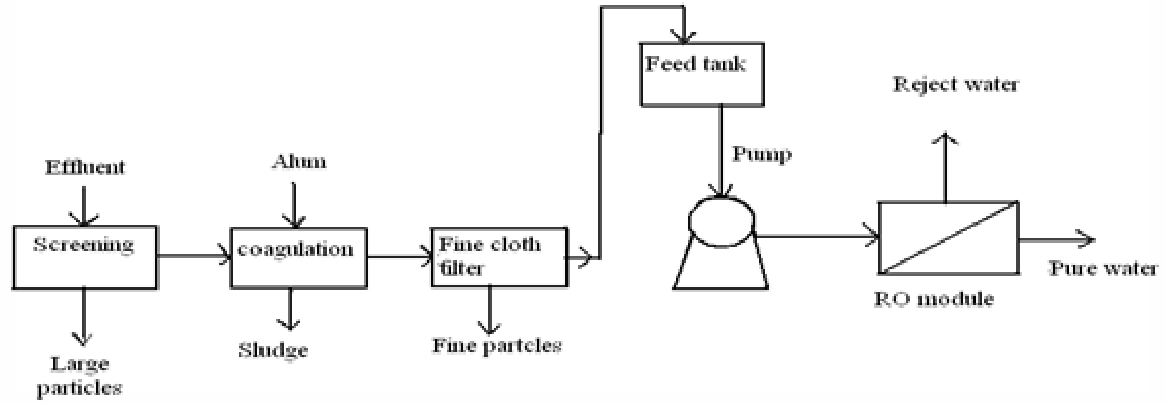

Fig. 1 Process flow diagram of treatment of tannery wastewater

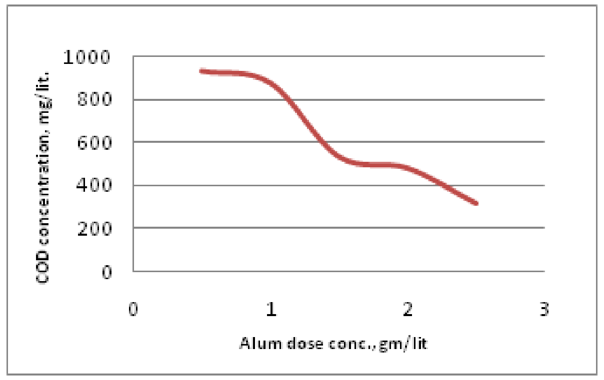

Fig. 2 Effects of alum dose on COD

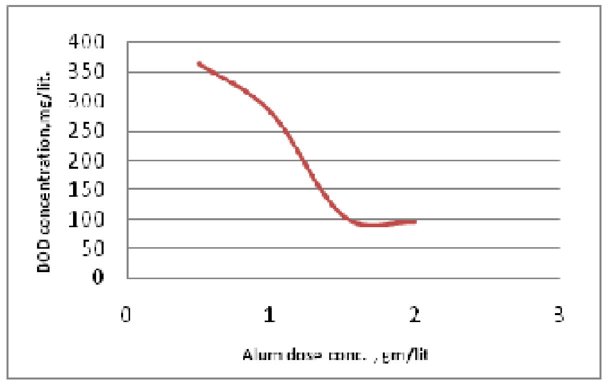

Fig. 3 Effects of alum dose on BOD

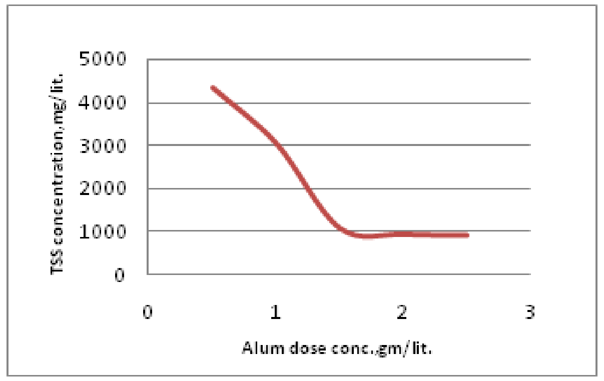

Fig. 4 Effects of alum dose on TSS concentration

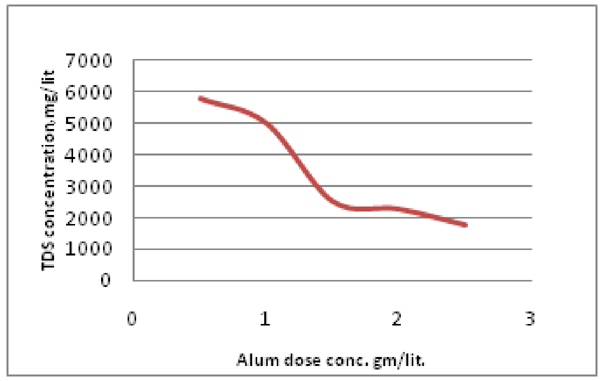

Fig. 5 Effects of alum dose on TDS concentration

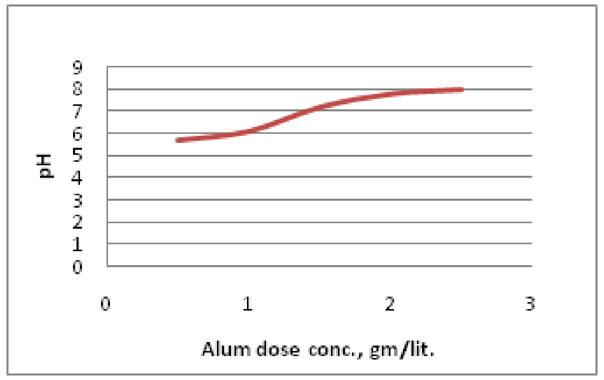

Fig. 6 Effects of alum dose on pH concentration

colorimetric method and COD, BOD, TDS, pH are measured by standard methods (APHA, 2005).

RESULT AND DISCUSSION

The supernatant of the pretreated effluent is taken out and various properties such as Chromium, pH, TDS, TS, BOD and COD are measured. The effluent is pretreated by screening to remove large floating and large suspended solids particles. Then after the pretreatment of the effluent characteristics are analyzed

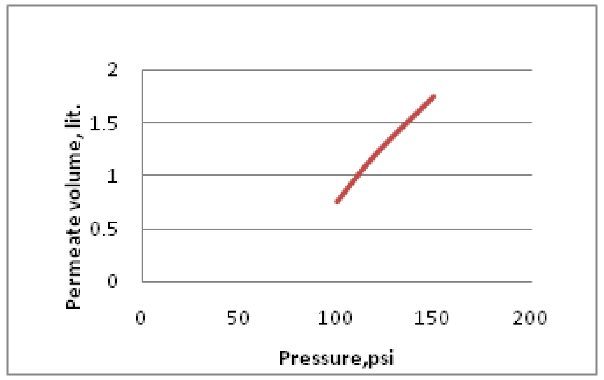

Fig. 7 Effects of permeate volume on different applying pressure

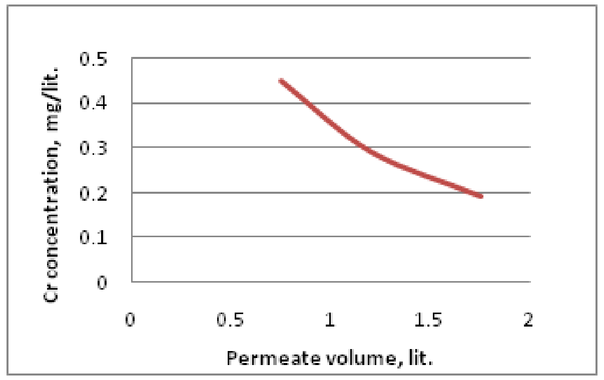

Fig. 8 Effects of chromium concentration on different permeate volume

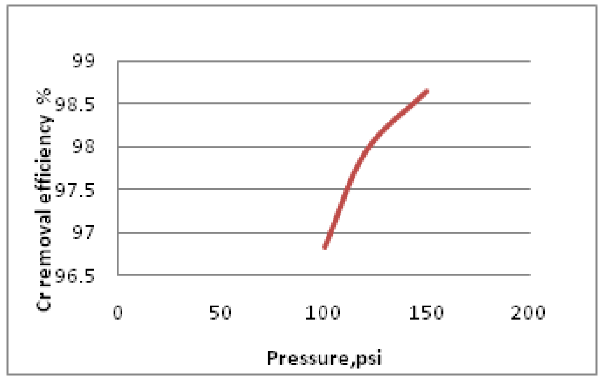

Fig. 9 Effects of chromium removal efficiency on different applying pressure

COD 1990 mg/L, BOD 512 mg./L, pH 4.9, TDS 7980 mg./L, TSS 9500 mg./L and chromium 14.2 mg./L.

The coagulant is determined by adding 0.5 to 2.5 g/L alum to the effluent and measuring BOD, COD, TDS, TSS and pH, at the different dose of alum.

When 0.5 gm/L alum dose added to the effluent suddenly the value of COD decreases 1960 mg/L to

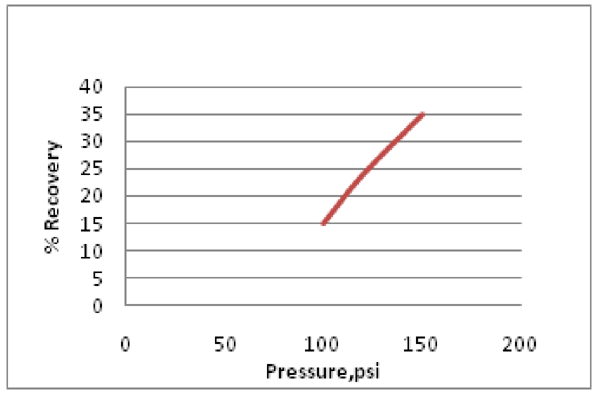

Fig. 10 Effects on % recovery on different applying pressure

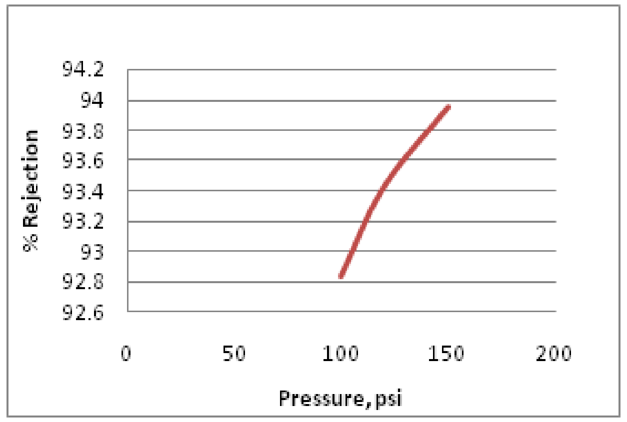

Fig. 11 Effects on % rejection on different applying pressure

1120 mg/L. Fig. 2 shows that COD concentration decrease 536 mg/L sharply with the increase in alum dose up to 1.5 g/L; but, the decrease is less for 2.0 to 2.5 gm/L. Higher dosages of alum.

Fig. 3 indicates that, at the 0.5 gm/L alum dose BOD concentration decreases up to 512 to 365 mg/L. After the 1.5 gm/L alum dose BOD is 105 mg/L but on 2.0 and 2.5 gm/L alum dose, BOD concentration has also minor change 95 and 79 mg/L respectively.

Fig. 6 indicates that, 0.5 gm/L alum dose added to the effluent suddenly the value of pH increases 4.9 to 5.7. Different alum dose to the effluent increases the value of pH, at optimum 1.5 gm/L dose pH is 7.2. After the 2.0 and 2.5 gm/L the pH value increase 7.8 and 8.0 respectively.

In the reverse osmosis treatment 5 L volumes of effluents fed to the reverse osmosis unit at different pressures to determine the optimum pressure at which sufficient permeates volume obtained. At 100,120 and 150 psi permeate volumes are 0.75, 1.2 and 1.75 L respectively. Fig. 7 shows that, when pressures are increased then permeate volumes are also increased.

The chromium concentration in the feed of reverse osmosis is 14.2 mg/L. At different pressures, different permeate volumes 0.75, 1.2 and 1.75 are obtained at which chromium concentrations are 0.45, 0.29, 0.19 mg/L respectively. Fig. 8 shows that, when the pressures are increased the permeate volume are also increased but because of high pressure chromium concentration decreases.

Fig. 9 shows that, at 100 psi pressure Cr removal efficiency is 96.83 % and at 120, 150 psi, efficiencies are 97.95 and 98.66 and respectively that means Cr removal efficiency also increases with various increasing pressures.

Cr waste may be seen in several other industries but the most concentrated effluents are discharged by tanneries. Moreover, they discharge large volumes of this toxic metal. In this experiment spiral wound module with thin film composite membrane is used. The RO system was operated to determine the optimized applying pressure (100, 120 and 150 psi), at which maximum Cr removal efficiency can obtained. The best treatment efficiency was obtained at 150 psi. It should be noted that at higher pressures the membrane resistance is also increased. Fig. 10 and Fig. 11 indicate that effect of % recovery and % rejection on applying pressures which are increased at pressures.

Optimum operating conditions was trans membrane pressure 150 psi, a feed flow rate of 10 L/hr and a feed temperature of 25 ^{o}C. The various properties of water measured after RO treatment COD 320 mg/L BOD 38 mg/L pH 7.6. The efficiency of Cr removal which was as high as 98.66% at the optimized conditions.

CONCLUSION

Removal of heavy metals dissolved at low concentrations in water and wastewaters is often a problem that can be solved in different ways. Application of reverse osmosis can be an effective way of heavy metal removal. Removal of Chromium (VI) from tannery wastewater has been studied using RO membrane. The RO unit used in this study was a spiral wound module with thin film composite membrane. The effluent is pretreated by screening to remove large floating and suspended solids which could interfere with the reverse osmosis operation. After the screening the effluent is sent to the coagulation. In the coagulation the effluent is kept in five 500 mL capacity beakers. The optimum coagulant is determined by adding 0.5 to 2.5 g/L alum to the effluent and measuring suspended solids. Therefore, 1.5 g/L is considered as the optimum alum dose at which COD 535 mg/L, BOD 105 mg/L, TSS 1095 mg/L, TDS 2515 mg/L and pH 7.2 are measured. After coagulation, the sludge settles at the bottom and the supernatant is siphoned out. Then, the clarified liquor is then treated reverse osmosis processes at different pressures 100, 120 and 150 psi for measuring optimum Cr removal efficiency. The best Cr removal efficiency of treatment wastewater by RO is 98.66 % at pH range of 5.6 to 7.2 and in temperature of about 25^{o}C at an applied pressure of 150 psi. Considering the efficiency of Cr removal which was as high as 98.66% at the optimized conditions and the characteristics of water are COD 320 mg/L. , BOD 38 mg/L, TSS 664 mg/L, TDS 464 mg/L and pH 7.6. It could be concluded that RO membrane process may be selected and developed as an effective alternative for treatment of metal contaminated effluents of leather and similar industries.

It could be concluded that RO membrane process may be selected and developed as an effective alternative for treatment of metal contaminated effluents of leather and similar industries. Since Cr is the most important element used to tannery industries are still considered to be the most leading sources of pollution of the environment to this metal RO has been widely applied to separate or concentrate aqueous solutions containing organics or salts . It involves separating water from a solution of dissolved solids by forcing water through a semi permeable membrane. As pressure is applied, larger molecules such as metal ions are retained by the membrane.

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