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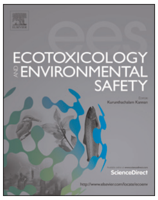

Nanofiltration based water reclamation from tannery effluent following coagulation pretreatment

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ABSTRACT

Coagulation–nanofiltration based integrated treatment scheme was employed in the present study to maximize the removal of toxic Cr(VI) species from tannery effluents. The coagulation pretreatment step using aluminium sulphate hexadecahydrate (alum) was optimized by response surface methodology (RSM). A nanofiltration unit was integrated with this coagulation pre-treatment unit and the resulting flux decline and permeate quality were investigated. Herein, the coagulation was conducted under response surface-optimized operating conditions. The hybrid process demonstrated high chromium(VI) removal efficiency over 98%. Besides, fouling of two of the tested nanofiltration membranes (NF1 and NF3) was relatively mitigated after feed pretreatment. Nanofiltration permeation fluxes as high as 80–100 L/m^2 h were thereby obtained. The resulting permeate stream quality post nanofiltration (NF3) was found to be suitable for effective reuse in tanneries, keeping the Cr(VI) concentration (0.13 mg/L), Biochemical Oxygen Demand (BOD) (65 mg/L), Chemical Oxygen Demand (COD) (142 mg/L), Total Dissolved Solids (TDS) (108 mg/L), Total Solids (TS) (86 mg/L) and conductivity levels (14 mho/cm) in perspective. The process water reclaiming ability of nanofiltration was thereby substantiated and the effectiveness of the proposed hybrid system was thus affirmed.

1. Introduction

Chromium is a common toxic heavy metal contaminant which is often disposed of into the environment through the effluents generated and discharged by various anthropogenic activities, such as chromium electro-plating, metal finishing, leather tanning, dye and textile industries (Chakraborty et al., 2014; Krishnani et al., 2013; Muthukrishnan and Guha, 2008). Cr(VI) oxidation state is relatively more hazardous and recalcitrant than Cr(III) state, owing to the high solubility and mobility of the oxyanion forms in which hexavalent chromium mostly exists, namely, chromate (CrO_4^{2-}), hydrogen chromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) (Wang et al., 2013). The deleterious ecotoxicological impacts of this priority pollutant on human health can be traced to its carcinogenicity (Chakraborty et al., 2014). Besides, it harms the skin, the respiratory tract, the liver, and the kidneys, and induces severe pulmonary congestions, diarrhoea and vomiting; it even damages the DNA, and thereby causes genetic deformations (Almaguer-Busso et al., 2009; Aoudj et al., 2015; Barrera-Díaz et al., 2012; Dalcin et al., 2011; Muthukrishnan and Guha, 2008). As such, the World Health Organization (WHO) and Central Pollution Control Board (CPCB), India have prescribed a maximum allowable limit of 0.1 mg/L for Cr(VI) concentration in effluents prior to their discharge into the surface waters (Bajpai et al., 2012; Wang et al., 2013).

Different procedures have hence been adopted with an objective to reduce the hexavalent chromium levels in the various industrial effluents to legislatively acceptable limits prior to their discharge into the environment. These treatment techniques include chemical methods involving chemically induced reduction and subsequent precipitation, electrochemical technologies, such as electrosorption, electrochemical reduction, and electrocoagulation–electroflotation, adsorption based processes, and biological techniques (Almaguer-Busso et al., 2009; Aoudj et al., 2015; Dalcin et al., 2011; Lakshmipathiraj et al., 2008; Liu et al., 2011; Qin et al., 2005; Ramrakhiani et al., 2011; Tan et al., 2015; Wang et al., 2015). However, there are several techno-economic bottlenecks, which considerably delimit the industrial viability of these treatment processes. For instance, the relatively cost-

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prohibitive and energy intensive electrochemical techniques, such as electrocoagulation, usually require perceptibly stringent monitoring of process parameters, while the electrochemical reactors that employ conventional or regular electrode materials are often marked by inordinately long process time, and relatively low current efficiencies (Almaguer-Busso et al., 2009; Barrera-Díaz et al., 2012; Wang et al., 2013). On the other hand, the physicochemical treatment processes involving adsorption are often marked by expensive regeneration of spent adsorbents and reduced adsorption efficiencies of the reactivated adsorbents (Dasgupta et al., 2014; Robinson et al., 2001). Besides, secondary waste products and sludge generation by conventional chemical precipitation based techniques, and the process inflexibilities demonstrated by bioremediation processes involving microorganisms, such as anaerobic and aerobic Cr(VI) reducing bacteria, are some of the commonly observed impediments to the successful application of these treatment techniques for Cr(VI) removal (Barrera-Díaz et al., 2012; Dasgupta et al., 2014; Liu et al., 2011; Wang et al., 2013).

The use of novel membrane-based separation processes in such cases can offer a technically as well as commercially feasible solution to the issues of clean treatment technology usage and process water reclamation, which the researchers and environmentalists are frequently confronted with. Various membrane based treatment processes, such as ultrafiltration, polymer enhanced ultrafiltration (PEUF), and nanofiltration are now in use for bringing about the successful removal of Cr(VI) species from contaminated wastewaters (Chakraborty et al., 2014; Muthukrishnan and Guha, 2008; Piedra et al., 2014). However, among all the membrane based methods explored till date, nanofiltration has emerged as a technologically superior innovation. Nanofiltration essentially lies between ultrafiltration and reverse osmosis from the perspective of the separation characteristics spectrum and the molecular weight cut off of a nanofiltration (NF) membrane ranges from 100 to 1000 Da. As such, it is able to bring relatively higher rejection of lower molecular weight solute components, such as heavy metals, as compared to ultrafiltration (Garcia et al., 2013; Piedra et al., 2014). The superiority of nanofiltration over reverse osmosis can be attributed to the various other advantageous aspects of nanofiltration, namely lower differential pressure driving force, lower consumption of energy, higher ion selective retention by the charged (positive or negative) NF membranes and higher solvent permeability (Dasgupta et al., 2014; Gherasim et al., 2013; Schäfer et al., 2005). These advantages account for the emerging popularity of nanofiltration in the field of industrial effluents treatment; the principal beneficiaries of nanofiltration include various chemical process industries, pulp and paper mills, textile industries and tanneries (Gozálvez-Zafrilla et al., 2008; Religa et al., 2011; Schäfer et al., 2005; Wang et al., 2011). It is worth mentioning in this regard that the efficacy of certain other futuristic membrane based processes, such as direct contact membrane distillation, for bringing about substantial mitigation of the heavy metal ion levels in process waste streams, has also been recently investigated (Zolotarev et al., 1994). Meticulous appraisal of archival literature reveals that these processes have demonstrated reasonable competence in removing heavy metal ions from wastewaters (Bhattacharya et al., 2014). However, these processes suffer from some serious disadvantages, which account for their relatively parochial application in industries. The membrane distillation process, for instance, are ordinarily marked by relatively low thermal efficiency and temperature polarization phenomena, which eventually lead to progressive reduction in the driving force for mass transfer (Chen et al., 2013; He et al., 2011). Besides, the membrane distillation processes are relatively complex and highly energy intensive, owing to substantial thermal energy consumption (Susanto, 2011). These techniques, moreover, employ hydrophobic membranes, which demonstrate an inadvertent propensity for fouling (Van der Bruggen, 2013). Nanofiltration, as a relatively energy-efficient and cost-competitive pressure driven membrane process, succeeds, albeit to a certain extent, in resolving these challenges (Chen et al., 2013; He et al., 2011; Susanto, 2011; Van der Bruggen, 2013; Van der Bruggen et al., 2008). As such, nanofiltration is often employed to bring about effective removal of toxic contaminants, such as heavy metal ions, from industrial effluents (Al-Rashdi et al., 2013; Gherasim and Mikulášek, 2014; Zhu et al., 2015).

However, the nanofiltration process also has its share of disadvantages, the primary impediment of the process being concentration polarization followed by NF membrane fouling and subsequent decline of flux with time; as a result the huge potential of nanofiltration remains largely untapped (Dasgupta et al., 2014; Van der Bruggen et al., 2008). This necessitates the selection of a suitable pretreatment process for the sampled effluent so as to reduce the feed load on the subsequent nanofiltration process. Coagulation is one such treatment technique which is frequently used in conjunction with nanofiltration, owing to its simplicity cost-effectiveness and reliability (Ellouze et al., 2012; Riera-Torres et al., 2010). However, overdose of coagulants, besides increasing the operational cost of the pretreatment process, also results in deterioration of the supernatant quality (Trinh and Kang, 2011). The optimization of process conditions as well as coagulant dose hence becomes an environmental imperative which ensures sufficient reduction of the target contaminant in the treated effluent; besides, it also strives to minimize sludge generation and addresses the perceptible problem of sludge disposal. This optimization can be conveniently conducted by employing a suitable statistical/mathematical tool such as response surface methodology (RSM).

The principal salient features of RSM are its flexibility and its ability to closely simulate real life problem environment through the incorporation of interaction effects in appropriate models (Cojocaru and Zakrzewska-Trznadel, 2007). The major sequential steps constituting the successful application of RSM are enumerated as: (1) statistically obtained design of experiments (DoE), involving concurrent variation of the adjustable process parameters over the prescribed set of experimental trials and examination of the results obtained. Therein in order to determine if the current settings of the independent variables are concordant with optimal response (2) reliable, near accurate mathematical prediction of the response function elucidating the relationship between target response (Y) and input process factors (X_is) by means of appropriate empirical models; (3) estimation of the coefficients in the models, and (4) statistical evaluation of the adequacy of the polynomial model fit (Chakraborty et al., 2014; Kumar and Pal, 2012; Myers et al., 2009).

In the present study, the efficiency demonstrated by a tailored coagulation–nanofiltration hybrid treatment scheme in removing hexavalent chromium was investigated. The optimization of coagulation pretreatment process was carried out using empirical models based on statistical paradigms prescribed by RSM. Additionally, comparative analysis was conducted between coagulation treatment unit and integrated coagulation–nanofiltration system in terms of their respective permeate qualities, in order to evaluate the viability exhibited by the hybrid process in generating treated effluent, which adequately satisfied the criteria for reuse and hence, could be conveniently reclaimed. Furthermore, the membrane fouling propensity in a nanofiltration process treating raw tannery effluent was also compared with that observed in the nanofiltration unit treating feed pretreated by coagulation. This investigation was carried out in order to explore the degree of membrane fouling reduction achieved through the application of the designed hybrid system.