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Application of nanofiltration membrane for treatment of chloride rich steel plant effluent

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ABSTRACT

Composite charged nanofiltration membrane of polysulfone and zinc chloride was used to treat the effluent from TATA Steel, India. The effluent contained high amount of total solid and various ions, namely chloride (1000–1200 mg/l), fluoride (140 mg/l), nitrate (37 mg/l) and phosphate (1730 mg/l). The effluent was pre-treated by passing over granular activated carbon and total solid was reduced by 38%. The membrane containing 1 wt% $ZnCl_2$ was found to be optimized one. Chloride concentration was reduced below 800 mg/l via charge–charge interaction by nanofiltration. Similarly fluoride, nitrate and phosphate ions were rejected around 32%, 27% and 70%, respectively. Effect of different operating conditions (transmembrane pressure, cross-flow rate and solution pH) was studied. Rejection of various ions and solid content was reduced with increase in transmembrane pressure and cross flow rate. Based on permeate flux and quality, 1380 kPa and 80 l/h cross flow rate were selected as optimum operating conditions. Simple in-situ washing of the membrane with tap water could recover permeate flux upto 97%. A resistance in series model was used to quantify the effects of polarization on system performance. This system can be scaled up in spiral wound configuration for final deployment.

1. Introduction

Contamination of surface water with different ions is a major environmental concern throughout the world [1]. In view of the fact that, only 3% of surface water is potable [2–5], increasing concentration of ions caused by industrial discharge, has posed itself as a serious threat to drinking water. Use of seawater in different stages of process industries increases chloride concentration in waste stream [6,7]. Among various ions, chloride has been reported to be most dangerous owing to its small size, high electronegativity and super-reactivity [8]. Eventually, it gets mixed up with surface water (pond, river, sea, etc.) through the water cycle and contaminates drinking water. Intake of chloride-rich water leads to damage of gill tissues of aquatic animals. Over exposure of chloride threatens human health, with risk of cancer [9].

Industries, especially, agricultural, petroleum, leather and steel require sea water for cooling, quenching, scrubbing, etc. As a result, wastewater from these industries becomes highly saline and rich in organic and inorganic materials [10]. One among seven steel production plants in India, Tata Steel, Jamshedpur uses upto 25 m^3 of water for per tonne of steel produced and volume of waste water is generated at the rate of 5 m^3/h [11]. Some physico-chemical processes are carried out to reduce load of organics from the effluent water. Coke oven by product water is treated by biochemical oxidation to remove phenol, cyanide, etc. Some part of the treated water is reused in the plant, rest being discharged to the environment. This water has high amount of chloride (1000–1500 mg/l) and also has high concentration of other ions (fluoride, nitrate, phosphate, etc.), high salinity, and total dissolved solid (TDS). Usage of sea-water for coke quenching can be identified as the origin for high chloride content and hence this water becomes corrosive for pipelines. It also poses serious threat to aquatic life. Thus, there is a requirement of efficient, less energy intensive and highly scalable technology to improve overall quality of the discharged effluent.

Ion exchange, biosorption, freezing, solar and geothermal desalination, distillation, are some of the commercially used

Abbreviation: BF, blast furnace; CFR, cross-flow-rate; FDR, flux decline ratio; FRR, flux recovery ratio; GAC, granular activated carbon; HCl, hydrochloric acid; IC, ion chromatgraphy; MPEGZ1, membrane with 1 wt% $ZnCl_2$; MPEGZ2, membrane with 2wt% $ZnCl_2$; MWCO, molecular weight cut-off; NaOH, sodium hydroxide; NF, nanofiltration; PANI, polyaniline; PSF, polysulfone; RO, reverse osmosis; TDS, total dissolved solid; TMP, transmembrane pressure; $ZnCl_2$, zinc chloride.

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Nomenclature

C_p	Solute concentration in permeate (kg/m^3)
C_F	Solute concentration in feed (kg/m^3)
k	Polarisation resistance growth constant
k_0	Model parameter defined in Eq. (8)
n_1	Model parameter defined in Eq. (3)
n_2	Model parameter defined in Eq. (3)
n_3	Model parameter defined in Eq. (8)
n_4	Model parameter defined in Eq. (8)
R	Rejection
R^2	Correlation coefficient
Re	Reynold's number
R_m	Membrane hydraulic resistance (m^{-1})
R_p^s	Steady state polarization resistance (m^{-1})
$R_p(t)$	Polarization resistance as a function of time (m^{-1})
v_w^s	Steady state permeate flux (m^3/m^2 s)
$v_w(t)$	Permeate flux as a function of time (m^3/m^2 s)
v_{wf}	Steady state flux (l/m^2 h)
v_{wi}	Initial flux of experiment (l/m^2 h)
v_{ww}	Pure water flux after washing (l/m^2 h)

Greek symbols

α	Model parameter defined in Eq. (3)
ΔP	Transmembrane pressure (Pa)
μ	Viscosity of effluent stream (Pa s)

techniques to reduce salinity [12–16]. However, low throughput and poor removal efficiency make these difficult for application in industrial scale. Membrane based separation processes offer alternative energy-efficient route. Reverse osmosis (RO), is a very popular technique for deionization and dechlorination [17]. Nevertheless, requirement of high transmembrane pressure (TMP), around 25 atm and low throughput, restrict large scale real life application [18]. Removal of small sized ions, by size exclusion, is difficult. Nanofiltration (NF) membrane can operate at lower TMP (10–20 atm) and offers higher throughput [19,20]. However, enhanced permeate flux limits the removal efficiency to 30–70%. Chloride and other ions, owing to their charged nature, can have some electrostatic interaction with charged surface. Imparting charges on surface of NF membranes may augment rejection of ions through charge–charge interaction, following Donnan exclusion principle [21,22]. Surface charge of a membrane can be enhanced by incorporating charge inducing agents, like metallic nanoparticle [23], conducting polymer (PANI), etc. [24]. This specific property can be fine tuned for targeted application [25]. Casting and characterization of polysulfone (PSF) based NF membranes have been reported [26,27]. Effect of different additives like poly isobutylene-alt-maleic anhydride, poly[(4-aminophenyl)sulfonyl]butane diamide, and methyalated poly[(4-aminophenyl)sulfonyl]butane diamide [26–30], etc., have been studied. Among various membrane materials, PSF offers an excellent choice, as it is stable in chloride solution at different solution pH [29].

In this work, composite NF membrane of polysulfone and zinc chloride has been used for treatment of industrial waste water, collected from clarifier tank, in the Tata Steel plant, Jamshedpur, India. After a pretreatment using granular activated carbon (GAC) [31], performance of this membrane has been studied at various operating conditions, namely at different TMP, cross-flow rate and pH. Optimum membrane and operating condition are selected, based on permeate quality and permeate flux. A simple resistance in series model is used to quantify the fouling of the membrane.

2. Materials and methods

2.1. Source of the effluent

Process for origin of the waste water, is presented in Fig. 1. During production of metal in a blast furnace (BF), hot air blast was blown to the furnace. After undergoing necessary chemical reactions, the flue gas came out from the top of BF. Temperature of this gas was high (120–370 °C). It was dust laden, rich in combustible gas and contained high amount of suspended solid (size upto 6 mm). This flue gas went through elaborate cleaning

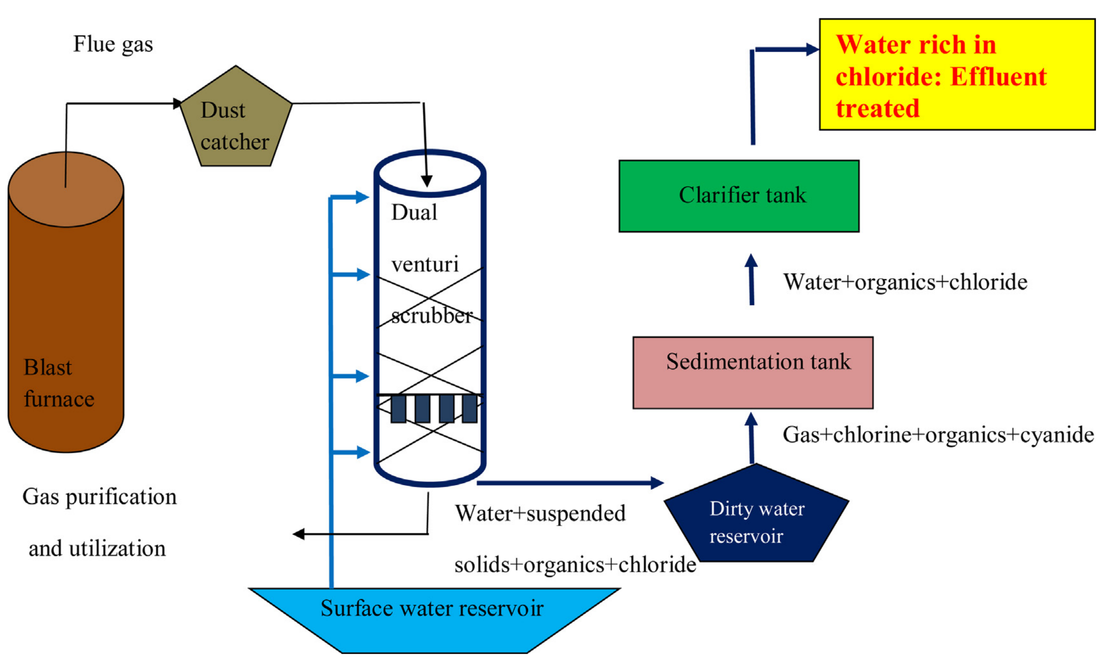

Fig. 1. Waste water generation process in Tata Steel, India.