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SCIENTIFIC PAPER

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A RESINS-NEUTRALIZATION COUPLED ROUTE FOR THE TREATMENT OF STAINLESS-STEEL PICKLING EFFLUENT: A RESEARCH STUDY

Article Highlights

- A cost-effective method for the conversion of Cr^{6+} into $Na_2Cr_2O_7$ using ion exchange resin
- Innocuous solids CaF_2, ZrF_4, $Zr(OH)_4$, $Fe(OH)_3$, $Cr(OH)_3$, and $Ni(OH)_3$ are safely discarded
- Nitrates are converted into $NaNO_3$ as the end product that can be recycled
- The presented strategy enhances the option of recycling pickling wastewater

Abstract

One of the major environmental problems caused by stainless-steel industries is the liquid effluents generated during the production processes. It contains a high concentration of metal ions such as Fe (III), Cr (III), Cr (VI), and Ni (II) in HF and HNO_3 *mixture, oil, and rinse wastewater. The used pickling waste stream has a pH of 0.5 and Total Dissolved Salts (TDS) of 520g/L with a density of 1.20g/CC. The present work focused on recycling pickling effluent by combining filtration, resins, and neutralization to remove metal ions efficiently and* F^- *greater than 99.5%. To remove TDS, laboratory experiments were performed using micro and ultra-filters with a membrane area 0.2m2. Cr (VI) was removed using TulsionFSMP 6301 resin and desorption using* $NaNO_3$ *and subsequent conversion into* $Na_2Cr_2O_7$ *as a by-product. For neutralization,* $Ca(OH)_2$ *and NaOH were used to precipitate metal ions, and the resulting filtrate was polished using* $ZrOCl_2$ *to remove* F^- *to 0.12 mg/L effectively. The nitrate was recovered as* $NaNO_3$*. Adsorption isotherm and kinetic studies were utilized for Cr (VI) from experimental data, and a process flow diagram was developed, which can eventually be tested on a larger scale.*

Keywords: Spent pickling solution, ion exchange, ultrafiltration, precipitation, industrial recycling, process flow sheet.

Metallurgical Industries of India (MII) use large quantities of aqueous acidic solution to treat stainless steel materials chemically. The treatment process primarily removes impurities such as stains, rust, scale, and other contaminants left on the steel surface. This process is referred to as acid pickling. The acidic bath is a mixture of hydrofluoric acid and nitric acid in demineralized (DM) water with 1:3:20 (v/v) proportions for the pickling of highly alloyed steels. The acids dissolve the metal oxide, forming a passivation chromium film layer on the steel surface. Lochyński *et al.* (2017) reported the XPS results on the surface morphology of passive film formation after pickling, resulting from increased chromium oxides and hydroxides in the passive layer [1]. After pickling, the steel surface is washed using water to remove the residual acid from the surface of the steel. Hydrofluoric acid reacts with the metal during pickling to form a fluoride complex. As the reaction proceeds, the acid concentration decreases with increased metal ion

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concentration in the pickling bath. Once the bath gets saturated with the metal, it cannot be used for further pickling operation, and the used pickling solution (UPS) is stored in tanks for disposal or treatment. Exhausted pickling lines and rinse water liquor contain soluble and insoluble metal salts of Fe^{3+}, Ni^{2+}, Cr^{3+}, and Cr^{6+} (with oxygen, it forms chromate [$Cr_2O_4^{2-}$] and dichromate [$Cr_2O_7^{2-}$], fluoride [F^-], and nitrate [NO_3^-]) as contaminants. Metallurgical industries using this route generate large quantities of UPS. Conventionally, the problem is addressed by neutralizing the UPS with calcium hydroxide. The lime reacts with hydrofluoric acid and nitric acid and forms calcium fluoride and calcium nitrate in an aqueous solution along with ferric, chromium, and nickel hydroxides, respectively, and the slurry mixture is filtered to separate the cake. The solid cake is dried and disposed of at a solid waste management facility for further disposal. If left untreated, the pickling wastewater containing toxic Cr^{6+}, F^-, and NO_3^-may leach into the ground and possibly contaminate groundwater [2–4]. According to Central Pollution Control Board (CPCB), pickling sludge and wastewater in India have been regarded as toxic waste and included in the hazardous waste list [5].

Over the last few decades, several processes were developed to treat these types of wastewater mixtures arising from pickling operations, such as acid recovery, recycling, and reduction of heavy metal concentration to an environmentally acceptable level. The methods include ion exchange [6–9], solvent extraction [10], evaporation and crystallization [11], distillation [12], diffusion dialysis, and electro membrane process [13,14]. Tang *et al.* (2018) reported the recovery of iron, chromium, and nickel from pickling sludge using a novel smelting reduction method [15]. The neutralization of UPS with calcium hydroxide produces calcium fluoride as solid waste, and the residual acid is neutralized. It hence cannot be recycled or used as by-products. Several studies have been carried out to solve this problem and reduce the toxic hexavalent chromium content in waste pickle liquor [16]. Relatively little attention was paid to converting mixed acid-metal pickle liquor into useful by-products. The use of membrane-based filtration and ion exchange resins plays a vital role in treating liquid effluents. In 1961, chelating ion-exchange resins were proposed to recover acids from metallurgical waste solutions [6]. Kobuchi *et al.* (1986) investigated the optimum operating conditions using diffusion dialysis and anion exchange membrane technology to recover hydrofluoric and nitric acids. The study outcome reported 100% recovery for nitric acid, 50%–60% recovery for hydrofluoric acid, and removal of more than 85% of ferric ions in mixed solutions [17]. Then, a continuous method for spent pickled liquor using an ion-exchange bipolar membrane and integration of dialysis allows the separation of acid and alkali, resulting in a recovery rate of 90% mixed acid (HF & HNO_3) [13]. A commercially developed ion-exchange technology named Recoflo® claimed improved exchange kinetics in separating mixed acid from metal salts [18]. Experimental investigation on the separation of iron from used pickling baths containing a very high concentration of hydrochloric acid using commercial ion-exchange cation, anion, and chelating resins was reported two decades back [7]. Marañón *et al.* (2000) established experimental assays using anionic resins for pickling water arising from the galvanizing process [19]. The ion exchange process was also used to recover chromic acid from mixed acid solutions [8]. Alguacil *et al.* (2004) examined and reported the removal of chromium (III) ions using ion-exchange resin from acidic waste solutions [9]. An investigation on the close loop circulation of rinse water after acid pickling in stainless steel was achieved using reverse osmosis, electrodialysis, and ion exchange [20]. Ultrafilter (UF) with a very low molecular weight cut-off (MCWO) was tested for retaining metal ions in the filter [21]. Ghare *et al.* (2014) employed commercially available anionic resin to remove iron from the UPS of hydrochloric and sulfuric acids [22]. An original contribution was established by Babu *et al.* (1993) for the removal of fluoride from pickling effluent in two stages using lime and zirconium [23]. A similar recent study also indicated fluoride removal by coagulation using zirconium tetrachloride as a complexing agent [24].

The main goal of this research was to study the application of ion exchange, membrane filtration techniques, and traditional neutralization to treat the mixed effluent generated from the pickling of stainless-steel production on a laboratory and bench scale. A thorough examination of the pickling effluent from an industrial site that produces nuclear-grade stainless steel materials with various compositions and different initial compositions was tested.

The use of ultra and microfilter, anionic ion exchange resin, calcium hydroxide, sodium hydroxide, and zirconium chloride was studied to treat effluent generated from the pickling process. The proposed research is of vital importance for industries handling mixed pickling effluents. The developed process eliminates Cr (VI) and subsequent conversion to sodium dichromate, compared to the current practice of neutralizing the effluents with lime and disposing of them as landfill, but for which the literature is not up to date. The end by-products from the process result in sodium nitrate, which is to be recycled for regeneration of ion exchange resin or sold, and the remaining by-products generated are safely disposed of as per the allowable limit under the pollution control board [5].

MATERIAL AND METHODS

In this study, laboratory and bench-scale studies were carried out using synthetic and real effluents from the industry, the process parameters have been fixed, and a flow sheet has been developed to recover nitrate as sodium nitrate. Sodium nitrate that is produced can be recycled back into the industry. The experimental protocol involves using a microfilter to remove suspended solids, anion exchange resin to remove Cr (VI), and recovery as sodium dichromate. Metal ions present in the effluent, such as Cr (III), Ni (II), and Fe (III), were precipitated as hydroxides using sodium hydroxide in the second stage. Simultaneously, calcium hydroxide was added to precipitate fluoride as calcium fluoride in the same solution. Polishing of fluoride using zirconium oxychloride was carried out in the final stage. The materials and techniques involved and the outcome of the results for the treatment mentioned above protocol are reported and discussed in this article. In addition, a detailed process flow sheet is provided for possible implementation in the industry.

Chemicals and experimental solutions

All the chemicals used in this study are analytical grade (AR) and directly used in the experiment as supplied by the manufacturer. The list of chemicals used, the supplier, and their purity are described in the following.

Synthetic effluent: Chromium nitrate nonahydrate (≥99.99%, SRL, India), Ferric nitrate (≥99.99%, SRL, India), Potassium dichromate (≥99%, Sigma Aldrich, USA), Nickel nitrate nonahydrate (≥99.99%, SRL, India), Nitric acid (Fisher Scientific, USA), Hydrofluoric acid (Fisher Scientific, USA).

Nitrate analysis: Orthophosphoric acid (Sigma-Aldrich, USA), Sulfanilic acid (≥99%, HiMedia, India), N-(1-Naphthyl) ethylenediamine dihydrochloride, NEDA (98%, SRL, India), Copper sulfate (99.9%, Sigma Aldrich, USA), Hydrazine sulfate (≥99%, Sigma Aldrich, USA), Sodium hydroxide (97%, Sigma Aldrich, USA), Sodium nitrate (99%, SRL, India).

Fluoride analysis: Sodium fluoride (≥99%, SRL, India), Zirconium oxychloride (≥99.5%, Sigma Aldrich, USA), Xylenol orange tetrasodium salt (≥99%, Loba Chemie, India), Potassium chloride (≥99.5%, SRL, India).

Hexavalent chromium analysis: Potassium dichromate (≥99%, Sigma Aldrich, USA), 1,5- diphenylcarbazide (DPC) (SRL, India ≥99% purity).

Neutralization chemicals: Calcium hydroxide (≥98%, SRIL, India), Sodium hydroxide (97%, Sigma Aldrich, USA).

The glassware used in the study was decontaminated by soaking it in a 5% (v/v) hydrochloric acid solution for 24 hours and rinsed with DM water.

Ion-exchange resin

The ion-exchange resins used in this study and their properties are enlisted in Table 1. The resin was washed with demineralized water to remove all impurities. The pretreatment of resin is performed with 4-bed volumes (BV) of 4% sodium hydroxide and washed with 7-BV of DM water, followed by 4-BV of 5% hydrochloric acid and washed with 7-BV of DM water to ensure complete pretreatment of the resin. The resin was dried at 60°C in an oven for 24 hours. The ion exchange capacity and the volume of resin required to treat per 100 mL of effluent are provided in Eq. (1) and Eq. (2), respectively. The anionic resins were eluted by using a desorbing agent (2N $NaNO_3$ and DM water) to evaluate the reusability of the ion-exchange resins and for the conversion of adsorbed dichromate into useful sodium dichromate as a by-product. About 0.5 g of adsorbent was stirred with 50 mg/L of the effluent for 3 hours using an orbital shaker for the desorption of hexavalent chromium. After equilibrium, the effluent concentration was determined. The effluent was then agitated with the eluent for the same duration as the reaction time of 3 hours [25]. After each treatment, the adsorbent material was separated from the reaction mixture and washed with DM water. Desorption experiments for Cr^{6+} ions were performed in the anionic (NO^{3-}) resin column. For equilibrium, adsorption experimental tests, 50 mL of stock solution was put in a flask, and 0.1 g of pretreated resin was added and loaded in an orbital shaker at 250 rpm for 60 minutes to ensure adsorption equilibrium [25,26]. The above-mentioned experimental tests were repeated for accuracy.

$$Ion-exchange\ capacity\left(\frac{meq}{g}\right)=\frac{NaOH_{ml}\times NaOH_{eq/_L}}{Mass\ of\ resin} \qquad (1)$$

$$\begin{aligned}&The\ volume\ of\ resin\ required\ per\ 100mL\ of\ effluent=\frac{4g}{100g}HF+\frac{10g}{100g}HNO_3=\frac{4}{20}\frac{1000geq}{100g/eq}+\frac{10geq}{63g/eq}\frac{1000meq}{100g}=\\&200+158=358meq\ per\ 100g\ of\ effluent\\&The\ volume\ of\ resin\ required=\frac{358}{IX\ capacity}=(x.)g\ for\ 100mL\ of\ effluent\end{aligned} \qquad (2)$$

Table 1. Characteristics of the ion-exchange resin

Resin type/design	SPL, macroporous, SBA	SPL, macroporous, SBA	Powder, SBA
Resin matrix type	Styrene DVB	Styrene DVB	Polystyrene, copolymer
Resin functional group	$-N^+R_3$	Quaternary amine	Quaternary ammonium type II
Standard ionic form	Freebase	Cl^- to OH^-	$Cl^-$to OH^-
Particle size, mm	0.3–1.2	0.55 ± 0.05	50 µm–75 µm
Moisture content, %	52–56	42–48	50 ± 3
Maximum operating temperature, °C	60	60	80
Total capacity, meq/mL	1.4	1.4	3.0
Resin name/Manufacturer	INDION, Ion exchange, India	Amberlite™ 4500CL, USA	Tulsion, FSMP 6301, Thermax, India

Instrumentation

To determine the concentration of iron, nickel, and chromium in the UPS and the treated solution, a flame Atomic Absorption Spectrophotometer (AAS), AA-301 (Thermo Fisher Scientific, USA) equipped with two hollow cathode lamps with individual power supplies was used. The AAS standards of Fe, Cr, and Ni were separately prepared from 1000 mg/L dissolved in 0.5N nitric acid (≥99.99%, SRL, India). The system control and output for recorded data were controlled by Thermo Scientific AA 301 software v.5.1. The AAS measurements were performed with the following conditions: Sample uptake rate: 7 mL/min; Air/acetylene pressure: 5 bar/2.6 bar controlled by rotameter and needle valve; Flame ignition: software-controlled; Fuel (acetylene): 7.66 L/min; Nebulizer: iridium; Spray chamber: nozzle inert; Wavelength range: Cr-357.9 nm, Fe-248.30 nm, Ni-232 nm; Detector: high-performance photomultiplier. A Shimadzu 160A UV-Visible spectroscopy with two quartz cells was used for measuring the concentration of hexavalent chromium at λ=540 nm, fluoride at λ=557 nm, and nitrate at wavelength, λ=220/275 nm in the synthetic, UPS, and treated solutions.

List of equipment used for bench-scale experiments

To prepare synthetic effluent and associated reagents, a 50-LPH reverse osmosis (RO) water plant coupled with a DM unit (Pervel Water Solutions, India) was set up for experimental studies. The DM water was produced upon pumping RO water (AJm75S 4 HP; Leo 3.0 Innovation, India) into two-separate poly-glass pressure vessels (1054 PENTAIR Structural™, India) loaded with 50 kg of cationic and 50 kg anionic ion exchange resins (Ion Exchange, India). The TDS of DM water was maintained between 3 and 6 mg/L, and the conductivity of the DM water (10-11.00 µS/ppm) was continuously monitored using an online controller (MS 623-HMD; Micro set Instrumentation & Controls Ltd, India). The ion exchange column was regenerated using a 5% hydrochloric acid solution for the cation exchanger and a 1% sodium hydroxide solution for the anion exchanger. The spent pickling solution was pumped from the storage tank to the membrane filter using a polytetrafluoroethylene diaphragm pump with a maximum dosing rate of 6 L/h at 4 kg/cm^2 pressure (Pro Aqua Chemical RO dosing pump Ltd, India). RO and UF technology was utilized in the removal of suspended solids. RO spun filters with 5 µm pore size, 25.4 mm length, and 60 mm diameter with the material of constructions [polypropylene (PP), polysulfone (PS), and polyethersulfone (PES)] inbuilt with cartridge, hollow fiber membrane module UF with 10 KD MCWO. The inlet feed and permeate flow rate were set at 6 L/m^{2}h and 3.5 L/m^{2}h. The area of the UF membrane is 0.2m^2, 1.4 mm OD, and 0.8 mm ID, which is packed with PES membranes inside the acrylic shell (TECH INC Incubating Technologies, India) and utilized for removing TSS in the UPS.

An ion exchange column was utilized in the adsorption of Cr (VI) in pickling wastewater [27]. The crystallization process for the formation of sodium dichromate solution in ion exchange regenerated liquid was performed in a high-temperature oven at 107 °C (Bio-Technics, India). The precipitation of iron, nickel, and total chromium in the form of hydroxides was achieved by mixing 5 eq/L caustic soda with 5 eq/L calcium oxide solution and adjusting the pH at 0.3 to 9.0. The hexavalent chromium-free pickle liquor precipitation was carried out in a volumetric flask using a magnetic stirrer (RSW 127; Royal Scientific, India) with various magnetic pellets. The pH in the precipitation process is carefully monitored using a pH meter (ECOTestrpH2; Thermo Fisher Scientific, USA) (0–14 pH) with ±0.1 accuracy, auto-calibration, and auto-buffer recognition. The filtration of the sludge precipitated with hydroxide was performed using a vacuum filter. The filtration of zirconium oxychloride treated liquid for fluoride removal was filtered using a Whatman paper (Grade 1).

Process steps involved in the recycling pickling waste

UFs were used to capture total suspended solids. Followed by an ion-exchange column [27] where the target Cr^{6+} ion was adsorbed by solid anionic resin, and the $Cr_2O_7^{2-}$ion was combined with Na^+ ions in the aqueous solution resulting in sodium dichromate through partial crystallization. The steps involved in the ion exchange process can be represented as follows given by equations 3 and 4:

$$\text{Adsorption}: 2R^{+} + Cr_2O_7^{2-} \rightarrow R_2Cr_2O_7 \qquad (3)$$

$$\text{Regeneration}: R_2Cr_2O_7 + 2Na^{+} \rightarrow 2R^{+} + Na_2Cr_2O_7 \qquad (4)$$

The exhausted ion-exchange resin column was regenerated using sodium nitrate solutions. A five-step process utilized in this study for treating the UPS is devised as provided in Figure.1

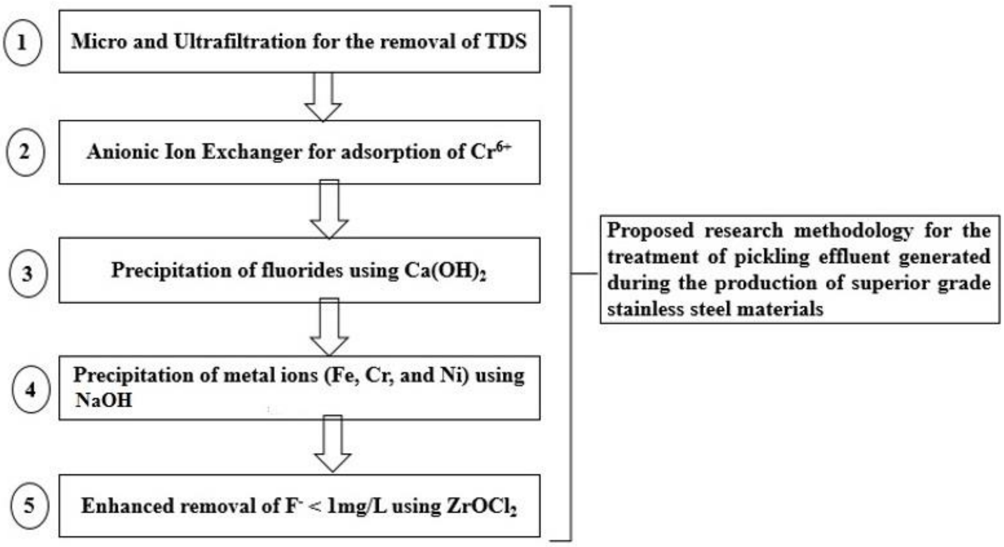

Figure 1. Experimental steps involved in the proposed research.

Bench-scale experiments

An experimental setup for verifying the process mentioned above steps was performed in this study, as shown in Figure 2. The pickling effluent contained suspended solids; hence, the liquid was filtered using a 5 µm micro filter and 10 kDa UF. The Microfilter and UF were fitted upstream to remove all the total suspended solids. A diaphragm pump controlled the UF flow rate. The selection of pump material was critical as the acidic medium passed through the pump, which was notoriously corrosive. In this study, the pump material is made from high-density polyethylene, which is non-corrodible and acid-resistant. The ion-exchange column loaded with resin was measured accurately using a weighing balance.

The permeate from the filtration process was collected and neutralized with mixed 5N NaOH and 5N $Ca(OH)_2$ solution in a conical flask using a magnetic pellet as a stirrer. The mixing has to be perfectly controlled so that all the metal ions, such as iron, nickel, and chromium in the permeate, get precipitated. Fluoride reduction was carried out separately using 100 mg/L zirconyl oxychloride solution in another conical flask using a magnetic pellet as a stirrer. The solution was added to the treated filtrate, the diluted 1 eq/L sodium hydroxide was added and stirred for 45 minutes, and the solution was left to settle for 24 hours. The clear supernatant solution was separated and analyzed for fluoride concentration, and the optimum pH was determined. This bench-scale process was repeated several times to collect sufficient data to generate the results for demonstration in the pilot scale.

Kinetic batch experiments were carried out using 50 mL of the stock solution put in a flask, and 0.1 g of pre-treated resin (Tulsion FSMP 6301, Thermax, India) was added and loaded in an orbital shaker (Scientech Technologies; SE-140, India) at 250 rpm at 26 °C. The solution was filtered, and the equilibrium concentration was determined using the 1,5-diphenylcarbazide (DPC) test [29]. The batch experimental tests were repeated several times for solutions of different initial concentrations to ensure sufficient data were collected for isothermal identification of hexavalent chromium adsorption by the NO_3^- resin.

Figure 2. Bench-scale experimental setup.

Working method for UV-Visible spectroscopic analysis

Determination of hexavalent chromium

The hexavalent chromium concentration in the UPS was determined by the DPC test [28,29]. The UPS and ion exchange treated samples were made up by adding an 8 mL solution with 2 mL DPC. The solution was kept still for 20 minutes to develop violet coloration and analyzed for hexavalent chromium. The calibration curve for concentration versus absorbance was plotted with a correlation coefficient, r^2, close to unity UFs.

Determination of nitrate

The nitrate concentration in the UPS was ascertained by N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) method [30,31]. Few modifications have been made in the experimental procedure for the accuracy of results. The experimental procedure is as follows: 1 mL of the sample to be analyzed was diluted to the 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, and 100 mg/L from the prepared 1000 mg/L sodium nitrate solution. Secondly, 2 mL of diluted sample was added with 1 mL of copper sulfate and hydrazine sulfate (reducing agent), 1 mL of sodium hydroxide solution, and 0.5 mL of coupling agent, which a heated and cooled to form pink solution, which is a mixture of orthophosphoric acid, sulfanilic acid, and NEDA. The reagents were mixed thoroughly and diluted with DM water, 5.5 mL making up a 10 mL solution. The solutions were mixed thoroughly and filtered using Whatman paper (Grade 1). The absorbance was measured at room temperature, and a calibration graph was plotted to obtain the concentration of the unknown sample using standard solutions with a correlation coefficient, r^2, close to unity.

Determination of fluoride

The fluoride concentration in UPS was examined by the xylenol orange test [32]. The experimental procedure was as follows: 15 mL of working standard and treated effluent, 5 mL zirconium oxychloride solution, and 2.5 mL of potassium chloride solution were mixed thoroughly. About 5 mL of xylenol orange solution was added by swirling the flask for 15 seconds. After 30 seconds, 25 mL of DM water was added, and the delivery break time should be approximately 7 seconds and repeatable. The contents were filtered using Whatman paper (Grade 1). The liquid was analyzed for fluoride concentration by constructing a calibration curve for concentration versus absorbance and plotted with a correlation coefficient, r^2, close to unity.

Equilibrium ion-exchange isotherms

The equilibrium isotherms describe how the adsorbent interacts with the adsorbate. The correlation of experimental results to the adsorption model can help to understand the adsorption mechanisms, the adsorbent surface heterogeneity, and its importance in the design and operation of adsorption [9]. A practical approach to the two and three-parameter adsorption isotherm models was chosen in this study. Two commonly used isotherm models, namely, Langmuir and Freundlich, were employed to describe the adsorption of chromium present in the effluent [8,14,33–35]. Sufficient data were collected for isothermal identification of Cr^{6+} adsorption by using NO^{3-}resin. The adsorption isotherm was executed from the bench-scale experiments. However, the results may be vital for performing adsorption and regeneration to evaluate pilot plant operations.

Langmuir isotherm

Langmuir suggested a theory to describe the monolayer coverage of adsorbate over a homogeneous adsorbent surface [8,33]. The adsorption isotherm is based on the assumption that sorption takes place at specific homogeneous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place at that site. Thus, an equilibrium value can be reached by using a linear Eq. (5).

$$\frac{C_e}{q_e}=\left(\frac{1}{q_m L}\right)+\left(\frac{C_e}{q_m}\right) \tag{5}$$

where C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity, i.e., the amount of chromium adsorbed on anionic resin beads (mg/g), and n is the isotherm constant.

The slope and intercept were determined by plotting C_e versus C_e/q_e, and the essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor Eq (6).

$$RL=\frac{1}{\left(1+LC_0\right)} \tag{6}$$

where RL is the dimensionless separation factor indicating the shape of the isotherm. L is the Langmuir constant related to adsorption energy, and C_o is the highest initial solute concentration.

By plotting the graph for C_e versus C_e/q_e, it was found that the R^2 value was in the range and approximately equaled 0.998. It was found the shape is linear. Therefore, the Langmuir isotherm fits the adsorption process as provided in Figure 3a. As the values of the synthetic effluent approximate that of the original effluent, the kinetics and isotherms were plotted only for the original effluent.

Freundlich isotherm

Freundlich suggested a model that describes the properties of heterogeneous adsorption systems, especially for organic compounds and highly interactive species on solid materials [8,33,34]. The studies from Freundlich showed that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant value at different concentrations. A multisite adsorption isotherm for heterogeneous surfaces is expressed as Eq. (7):

$$\log q_e=\log k_e+\frac{1}{n}\log C_e \tag{7}$$

where k_e and n are the Freundlich constants, Q_e is the ratio of the mass of adsorbate and mass of adsorbent, and C_e is the equilibrium concentration of the adsorbate.

The higher the n value, the stronger the adsorption intensity. The Freundlich constants were determined from the slope and intercept by plotting log q_e versus log C_e. The Freundlich isotherm model fit reveals that the adsorption of Cr^{6+} has a negative slope, as seen in Figure 3b, and the R^2 value is higher for the Langmuir isotherm model when compared to the Freundlich isotherm model. Therefore, Langmuir isotherm best suits the adsorption process. The isotherm parameters using the model fit are listed in Table 2. It can be inferred that those values of R^2 are greater than 0.985. These adsorption isotherm parameters allow easy identification of equilibrium ion exchange of anionic-based resin for different initial conditions.

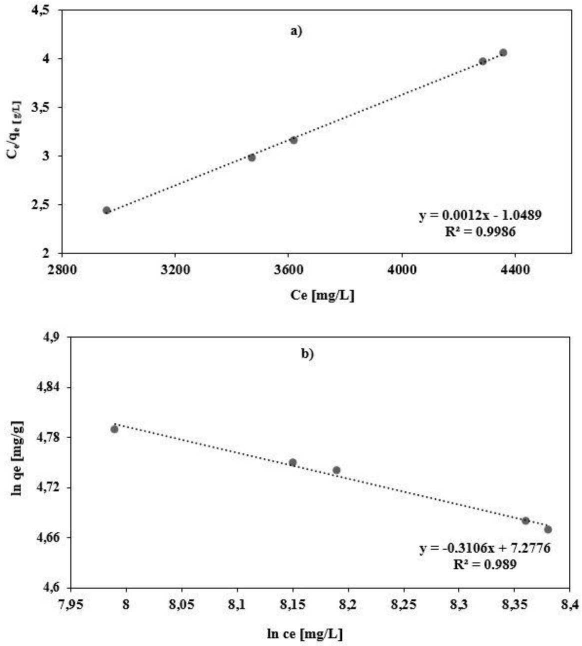

Figure 3. Langmuir (a) and Freundlich (b) isotherm for adsorption of chromium (VI) by anionic ion exchange (NO_3^-) resin.

Table 2. Adsorption isotherm parameters and linear regression coefficient, R^2.

	Langmuir			Freundlich		
	Q_m (mg/g)	R_L	R^2	K	n	R^2
Pore size (ϕ)	833.33	0	0.998	19.79	3	0.989

Kinetic studies

Kinetic models such as the Lagergren first-order, pseudo-second-order kinetic, Elovich, and intra-particle diffusion models were used to evaluate adsorption kinetics and rate-limiting steps. To investigate the suitability of pseudo-first-order Eq. (8) and second-order Eq. (9) kinetic models for the adsorption of hexavalent chromium, the Lagergren equation was utilized in this study [8,34,35].

Pseudo-first-order equation is given as:

$$\ln\left(q_e-q_t\right)=\ln q_e-k_1 t \tag{8}$$

where k_1 is the pseudo-first-order rate constants (min^{-1}), q_e and q_t are the amount of hexavalent chromium adsorbed (mg/g) at equilibrium, and time, t (min), respectively.

From the numerical analysis, the value q_e of 56.13 mg/g does not match the theoretical value of 43.584 mg/g. Therefore, it was observed that this process does not follow a pseudo-first-order reaction, as shown in Figure 4a.

Pseudo-second-order equation is given as:

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{t}{q_e} \qquad (9)$$

where k_2 is the pseudo-second-order rate constant (g/mg·min), q_e and q_t are the amounts of hexavalent chromium adsorbed (mg/g) at equilibrium and at the time, t (min), respectively.

From the numerical calculations, the value of q_e= 49.75 mg/g and k_2=0.0122 g/mg min, which almost approximates the theoretical value of q_e= 43.584mg/g, and R^2 value is close to unity in second-order kinetics as provided in Figure 6. Therefore, it can be suggested that the experimental data accurately support the best fit from the pseudo-second-order kinetic model for the adsorption of hexavalent chromium on anionic resin beads.

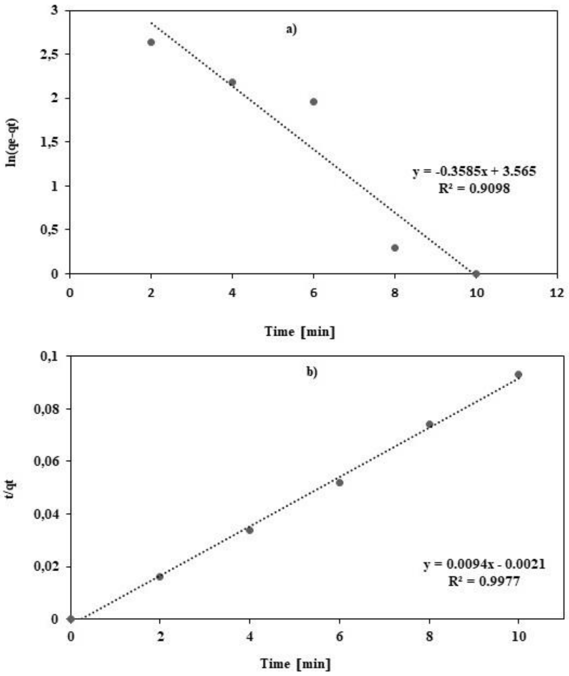

Figure 4. Pseudo first-order (a) and second-order (b) kinetics for adsorption of chromium (VI) by anionic ion exchange (NO_3^-) resin.

RESULTS AND DISCUSSION

The results obtained from the bench-scale experiments are discussed to understand the behavior of synthetic and actual pickling effluent for the treatment methods discussed above. The chemical composition of pickling effluent, prefiltering of pickling waste, hexavalent chromium removal by anionic ion exchange, desorption of hexavalent chromium, hydroxide precipitation of fluorides and metal ions (Fe (III), Cr (III), Cr (VI), and Ni (II)), secondary removal of fluoride using zirconium oxychloride and treatment process flow sheet for pilot scale demonstration is discussed in this section.

Characterization of pickling effluent

Pickling effluent of various lines from a metallurgical site in India was characterized and observed over time. Experimental investigations were performed to characterize the pickling effluent concerning its chemical composition: metal content (total Fe, Cr, and Ni), NO_3^-, F^-, pH, total dissolved salts, and total suspended solids.

Prefiltering of pickling waste

Two types of microporous membrane filters made from 5 µm pore size polypropylene (PP) and 5 µm polysulfone (PS) and a UF with 10 kDa pore size made of polyethersulfone (PES) were tested in the filtering of suspended particles removal in the effluent. The primary filtration was carried out using microporous membrane filters (a,b) and secondary filtration using UF (c) filter for further removal of finer particles that escaped the first microfilter. After experimentation, it was found that it is possible to remove 50% of primary suspended particles by employing a PS-based micro filter and up to 99.95% of suspended solids using PES UF. The prefiltration experimental trials were conducted using actual effluent from a pickling bath. A 20% reduction in solid content was observed using a polypropylene (PP) micro filter and a 50% reduction using a polysulfone micro filter. The addition of polyethersulfone (PES) based ultra-filter in this study achieved 99.95% removal of total suspended solids. Schmidt *et al.* (2007) [20] experimented with microfiltration as a prefilter to separate contaminated rinse water regeneration in steel pickling. Our study utilized the enhancement of microfiltration with ultrafiltration gave better efficacy for removing total suspended solids. It was found that 5 µm polyether sulfone has higher efficiency compared to 5 µm polypropylene.

Removal of Cr^{6+} using anion exchange process

An ion-exchange technology was used for the removal of hexavalent chromium. The decrease in Cr^{6+} concentration to permissible limits was achieved after passing the effluent for four cycles in the ion exchange resin. Exactly 1.0 mL of effluent was collected after every cycle and analyzed for Cr^{6+} concentration. This process was repeated several times to verify the ion exchange-resin efficacy. The resin in the form of anionic resin was utilized to adsorb the anionic chromium in the form of dichromate and thus exiting only the remaining metal ions. The retained Cr^{6+} in the ion-exchange bed was eluted using sodium nitrate and sodium hydroxide to convert into sodium dichromate using partial crystallization. The ion exchange process was carried out for four cycles in three columns with three different resin materials equally distributed. Among the three resins utilized in this study, the highest efficiency was observed in Tulsion, FSMP 6301 Thermax resin, as provided in Table.1. After experimentation, it was found that Thermax resin had the lowest Cr^{6+} exit concentration of 0.14 mg/L. The other two Amberlite™4500CL, USA, and the INDION, Ion exchange, India resin materials had Cr^{6+} exit concentrations of 3.79 mg/L and 6.79 mg/L, respectively. It occurred due to the low porosity and high resin affinity with a smaller surface area to adsorb the dichromate ions. Earlier studies revealed the use of anionic resin (OH-type, Ambersep 900) for the adsorption of dichromate ions and converting it into chromic acid using strong base cationic (H-type, Ambersep 132) resin. The effective ion-exchange adsorption of Cr^{6+} using ion exchange for Na^+ was reported in their study. The study illustrates that the complete desorption of Cr^{6+} in ion exchange is strongly dependent on a high feed flow rate and regeneration with a low flow rate [8].

Similar ion exchange resins were used to remove iron ions (Fe^{3+}) from pickling wastewater with hydrochloric acid. It is reported that Fe^{3+} ions were removed by anionic complexes using chloride anion. It is to be noted that anionic resins with complexing agents are highly efficient in the removal of iron, using Lewatit MP-500 resin up to 6 mg/L. Also, the exchange capacity increased with metal concentration. A low flow rate of 10 mL/min with elution carried out using 2.5-BV of water was observed from the earlier study. Marañón *et al.* (2000) [19] extended the above study using two different anionic resins, namely Lewatit MP-500 and Lewatit M-504, to remove Fe^{3+} and Zn^{2+} from HCl pickling bath. The test results demonstrated a very high capacity for removing Zn ions. The retained metals in the resin were eluted with DM water with 3-BV for iron and 6-BV for zinc. For both cases, it was reported that the decomposition of the metals retained chloro complexes releasing $ZnCl_2$ and $FeCl_3$. The resins were dissociated to chloride form to be reused again.

Desorption of hexavalent chromium

The economic feasibility of the adsorption process deals with the regeneration of the spent adsorbents in pilot plant operation. The study was performed in a strong base anionic resin Tulsion, FSMP 6301, as it had a higher affinity for the adsorption of hexavalent chromium than the other two resins employed in this research work. The percentage adsorption in each case was computed by using the following relation (10):

$$\%\ adsorption = \frac{Concentration\ of\ desorption, C_{des}}{Concentration\ of\ adsorption, C_{ads}} \tag{10}$$

C_{des} and C_{ads} (mg/L) represent the effluent concentration in desorbed and adsorbed phases, respectively. Three experiments were employed to study the desorption of Cr (VI) resin using sodium nitrate and rinse water. All the experimental trials exhibited similar characteristics. From the mass balance of desorption studies, it was evident that 97.78±0.1% of hexavalent chromium accumulated inside the column was effectively removed using sodium nitrate.

The formation of sodium dichromate after passing the 5 eq/L sodium nitrate solution through the column was observed in this study. The resulting liquid was collected and evaporated at 107 °C in an oven. The evaporation of dichromate liquid was continued till the liquid reached the supersaturation state. The formation of dichromate began when the liquid reached the supersaturation stage. Hence the liquid was heated to reach its supersaturation stage. The initiation of crystal formation was detected as sodium dichromate crystals. The crystals grew when evaporation was further continued. This process was repeated for several days in the oven to obtain a few grams of sodium dichromate crystals. The presence of sodium in the desorbed liquid was verified using a flame photometer. It is noted that this is a cyclic process, and adsorption regeneration takes an enormous time to produce a bulk of sodium dichromate materials. It was consistent with the theoretical prediction for converting hexavalent chromium into sodium dichromate.

Hydroxide precipitation of fluoride and metal ions

The effect of pH is an important parameter controlling the uptake of fluoride and heavy metals from an aqueous solution. The Atomic Absorption Spectrophotometer (AAS) results of neutralization in the filtrate were studied in the pH range of 6.0–9.0. The precipitation of fluoride in the form of calcium fluoride is achieved by first adding 5 eq/L slaked lime solution from pH 0.3 to 2.0–2.5. Simultaneously, a 5 eq/L lye solution was utilized from pH 2.0–2.5 to 7.0–9.0 to achieve hydroxide precipitation of metal ions (Fe, Cr, and Ni). The effect of pH on the F^-, Fe, Cr, and Ni ions was tested at pH values ranging from 0.3 to 9.0 in this study. It was found that the optimum pH for removing metal ions lies between 6.0 to 8.0.

Results showed that the addition of lime and lye to effluent influenced the reduction of calcium fluoride at pH 2.0–2.5 and hydroxide precipitation of metal ions (Fe, Cr, and Ni) at pH 7.0–9.0. From experimental results, it was observed between pH 0.3 and 2.0, the precipitation of calcium fluoride tends to be slower with excessive slaked lime addition, and from pH 2.0 to 9.0, the hydroxide precipitation of metal ions (Fe, Cr, and Ni) tends to be faster with less lye addition. The initial pH value from 0.6 to reaching pH 2.0 took 45 minutes using slaked lime. It was observed the pH quickly increased in less than 15 minutes retention time from pH 2.0 to 7.0 under lye addition. The time duration was averaged from several experimental trials. When the absolute value of the pH is at its highest, the precipitation retention time is lowered with a faster neutralization reaction. The results of pH balance versus time from the addition of slaked lime and caustic soda are provided in Figure 5.

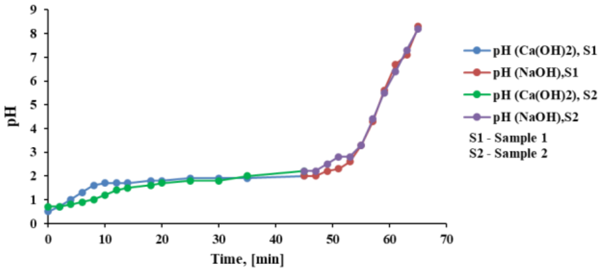

Figure 5. Addition of slaked lime and caustic in the effluent for pH balance after filtration and ion exchange process.

The neutralization of pickling wastewater has been vastly investigated by several investigators ever since the stainless-steel pickling process was implemented. The most common and traditional method for treating pickling wastewater is neutralization. The pH was increased, and most of the metal ions were precipitated, forming metal hydroxide sludge. The sludge can be safely discarded, but not the filtrate, since they contain a high nitrate concentration above the allowable limits. In the current environmental problems, wastewater treatment generated from the pickling process has become an area of interest. The disadvantage of only using the neutralization technique for pickling effluent is that the nitrate content in water is not reduced. It has led to further development and treatment methods for nitrate reduction [36]. In this study, neutralization treatment is used partly to remove metal ions (Fe, Cr, and Ni), and fluorides and nitrates were recovered.

Removal of fluoride using zirconium oxychloride

Zirconium oxychloride was employed to remove the fluoride in the separated filtrate. The primary filtrate from the neutralization process was polished using a zirconium chloride solution. The concentration of the polishing $ZrOCl_2$ solution, in addition to the separated filtrate, is dependent on the fluoride concentration from the previous neutralization process. It was tested to reduce the fluoride content from <10 mg/L to <0.2 mg/L in the treated filtrate using 100 ppm $ZrOCl_2$ solution from the actual effluent. The results were in concordance with Babu *et al.* (1993) [23], indicating the potential removal of fluoride in pickling wastewater with <100 mg/L, and F^- concentration drastically reduced to 0.12 mg/L using zirconium. The earlier study indicates that the zirconium hydroxide precipitate formed can be quantitatively removed using dilute sodium hydroxide. The present study reports an optimum pH level of 8.3 and 8.2 in the actual and synthetic polished filtrate. The final treated liquid contains sodium nitrate, which is used to regenerate the ion exchange column or can be sold for industrial use (e.g., bleaching agent). Also, a recent study by Gan *et al.* (2019) [24] experimented with the mechanism and performance of zirconium tetrachloride to remove fluoride using aluminum sulfate as a coagulant. The optimum pH was between 4.0 and 6.0 for the zirconium tetrachloride complex and between 8.0 and 10.0 for the zirconium aluminum sulfate complex. Their results also highlighted the use of the Zr-F complex as a superior material considering the Al-F complex as the resulting solution also showed a lower residual concentration of metal ions. The summary of results from this novel treatment process for treating the effluent generated during the pickling of stainless steel products is provided in Table 3.

Limitations of the proposed system for pilot scale demonstration

While scaling up the proposed process, the following limitations are to be considered. The condition of the micro and ultra-filters, ion exchange resin, and the best time to clean it. The replacement of poly sulfone micro-filter and polyether sulfone-based ultra-filter. The resin samples employed in the process shall be periodically checked for their physical and chemical stability, resin fouling, and clogging leading to channeling. Maintaining the concentration levels of metal ions in the pickling effluent. New ion exchange efficiency versus used ion exchange capacity may lead to inconsistent results.

Theoretical pilot plant calculations and economic benefit analysis

The volume of pickled waste per year at SSTP = 100 kL. The volume of pickled waste per month at SSTP = (100000 L)/12=8333.33 liters of pickled liquor. Commercial pilot plant operational days in a month = 20.

Number of liters to be treated per day= 8333.33/20 = 416.66 L/day. Approximately 70 L per hour for 6 hours of operation in a day. Pilot plant operation for techno commercial viability = 20 x 12 = 240 days/year = 240 x 24 = 5760 hours of operation per year. Demonstration pilot plant is 1/5 th of original plant = 70 L/hr = 14 to15 L/hr, operation per day = 84 L/day. Ion exchange capacity = 3 meq/g. Cr^{6+} concentration = 4.3 g/l = 4.3/51.99 = 0.082 meq/l × 150 = 12,450(meq/1000) = 12.5/3 = 4.13 = 5 kg. One week operation = 5 kg × 5 batches = 25 kg. At 60% utilization of anionic bed = 25/0.6 = 41 kg = 40 to 50 L resin column. Five batches of pickled waste to be treated 5 × 132 L = 660 L. After five batches of regeneration using 3 N $NaNO_3$, 12.5 eq Cr^{6+} to $NaNO_3$ = 12.5/3N = 4.2 L of theoretical regeneration. 20 L of 3N $NaNO_3$ to be used for regeneration after five operation cycles. 20 L of DM water, 50 L evaporator, and crystallizer (once in-week operational). The concentration of metal ions, fluoride, and nitrate on an industrial scale is provided from experiments. 70 g/l of F^- for CaF_2 = 78/(19 × 2) × 70 = 140. 11.7 g/l of Cr^{3+} for $Cr(OH)_3$ = 105/51.99 × 11.7 = 24 g. 70 g/l of Fe^{2+} for Fe $(OH)_3$ = 107/55.84 × 70 = 134 g. 25 g/l of Ni^{2+} for $Ni(OH)_2$ = 93/58.69 ×25 = 40 g. Total hydroxides = 140 + 24 + 134 + 40 = 338 g/L. Effluent treatment per batch = 84 L/day. Total hydroxides = 84 L/day × 338 g/L = 28,392~30 kg solids. Fluoride conversion to ZrF_4 = 100/1000 g/L × 132 × 167/(19 × 4) = 29 g/batch = 0.03 kg/batch. Total nitrate = 120 g/L. Per batch about 14 L = 120 x 14 = 1680 g. 90% recovery = 1680 x 0.9 = 1512 g. $NaNO_3$ in the treated effluent =1512/30 g/L = 50.5 g/L = 50.5 x 84/62 = 70 g/L as $NaNO_3$. To find out the amount of sludge produced in the precipitation/clarifier tank, we consider the following chemical reaction taking place inside the effluent bath for neutralization:

$$2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$$
$$Fe(NO_3)_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaNO_3$$
$$Cr(NO_3)_3 + 3NaOH \rightarrow Cr(OH)_3 + 3NaNO_3$$
$$Ni(NO_3)_2 + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3$$

A stoichiometry balance was calculated to determine the total sludge produced for neutralization consideration. Total sludge produced for 1 L of the effluent = 381 g. For 22 L of effluent per day (pilot plant), 7.2 L of NaOH and 1.7 L of $Ca(OH)_2$ are required to neutralize the effluent. The total volume of neutralizing agent is ~16 L.

From the above calculations, the initial cost in establishing the pilot plant cost, i.e., the present value of the future benefit, is between ₹.10 Lakhs to 20 Lakhs, i.e., \$12,500–\$18,500, on average, \$15,500. The present value of the future costs will be approximately \$10,500 by selling bulk chemicals from recycling.

The net present value (NPV) = Σ Present value of future benefits - Σ Present value of future costs = \$15,500–\$10,500 = \$5000. Since the NPV is positive, the project shall be executed.

Table 1. Pickling effluent concentration before and after treatment with discharge limits [4].

Pollutant species	Concentration before treatment	Concentration after treatment	Concentration before treatment	Concentration after treatment	Permissible limit
	Original effluent		Synthetic effluent		
Iron, mg/L	179074	1.55	133500	0.58	3.0
Chromium, mg/L	27285	1.78	27252	0.14	2.0
Hexavalent chromium, mg/L	100	0.14	66	0.06	0.1
Nickel, mg/L	24070	1.29	15007	1.83	3.0
Fluoride, mg/L	69540	-	65500		15
Fluoride (Stage I, neutralization)	-	9.37	-	10.86	-
F^-, pH	-	5.3	-	5.1	-
Fluoride (Stage II, $ZrOCl_2$ polishing)	-	0.12	-	0.19	-
F^-, pH	-	8.3	-	8.2	6.0–9.0
Nitrate, mg/L	81450	52333	79950	46650	10
pH	0.50	8.3	0.30	8.2	6.0–9.0
Density, g/CC	1.20	1.10	1.10	1.09	
TDS, mg/L	520000	-	-	-	-
TSS, mg/L	72000	-	-	-	-

Flowchart for treatment of pickling waste

Based on the process mechanism for treating the UPS, a process-flow sheet was developed and schematically represented in Figure 6. A single-packed column of (NO^{3-}) type resin (50 kg) will be employed in the ion exchange column. The metallurgical plant at the site generated about 100 kL of spent pickling effluent per year. The volume of spent liquor per month was about 8340 L. A plant with 20 days per month of operation was envisaged. About 416 L of spent waste was treated daily with 70 L per hour for 6 hours of batch operation a day. The techno-commercial viability of plant operation was about 5760 hours per year, an operation of 240 days per year. The remaining 125 days were left for plant maintenance. The process started with pickling waste solution entering the micro-filter and UFs, where the total dissolved salts were captured. Second, the filtered liquid was passed through the resin column, where the dichromate was adsorbed onto the solid phase by NO^{3-}ions. The ion-exchange operation continued until the Cr^{6+} concentration in the exit aqueous solution exceeded the direct discharge limit of 0.1 mg/L [5].

As the resin was in nitrate form, hexavalent chromium adsorbed onto the resin was converted to sodium dichromate solids using a partial crystallization process at 60 °C. The remaining liquid entered the precipitation tank where much of Cr^{3+}, Fe^{3+}, Ni^{2+}, and the bulk of F^- was precipitated to metal hydroxides by mixed addition of $Ca(OH)_2$ and NaOH and by adjusting the pH from acidic pH < 1.0 to base pH <9.0. The precipitated sludge was passed through a rotary filter to separate solid-liquid and toxic-free solids and was sent to disposal. $ZrOCl_2$ solution was prepared and added to the treated filtrate; dilute sodium hydroxide was added and stirred, and the solution was left to settle for 24 hours. The clear supernatant solution was drawn for fluoride analysis, and the optimum pH was determined. It was done to reduce the fluoride discharge levels to <1 mg/L in the treated effluent [22]. The solids zirconium fluoride and zirconium hydroxide formed in this process were removed. The final treated liquid contained only $NaNO_3$ solutions which were to be recycled.

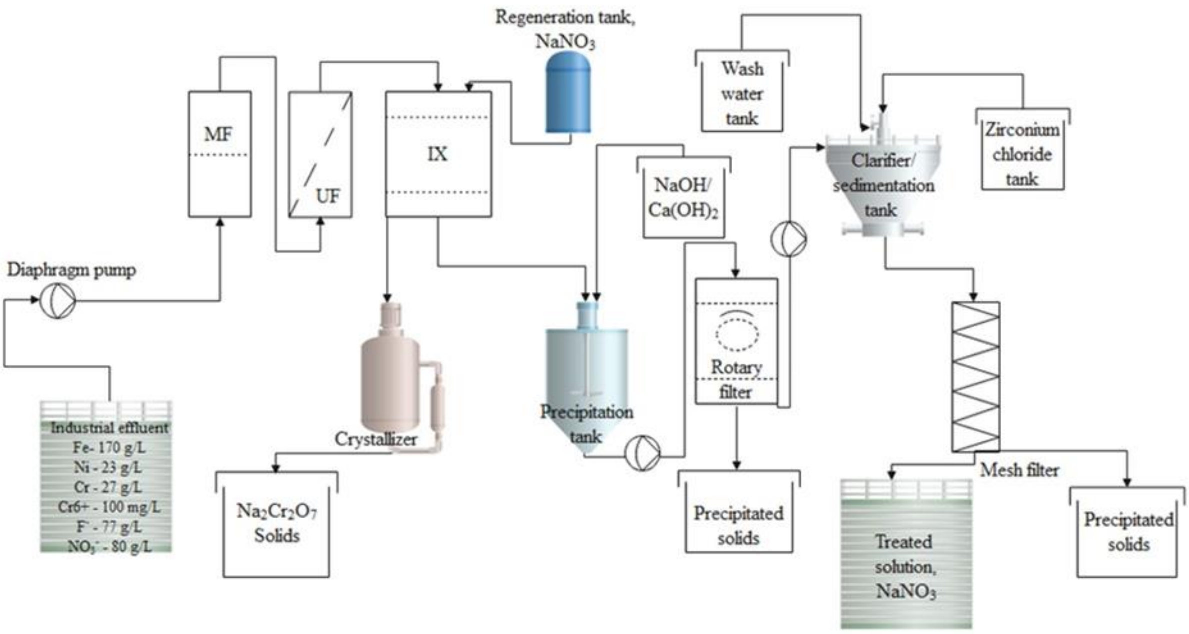

Figure 6. Developed process flow sheet for recycling used pickling wastewater.

CONCLUSION

Bench-scale experiments combining filtration, ion exchange process, and neutralization were utilized to treat pickling effluent. In step I, micro and ultrafiltration indicate a 99.95% removal of TSS/TDS. In step II, the ion exchange resin efficiently adsorbed Cr^{6+} and desorbed as $Na_2Cr_2O_7$ using $NaNO_3$ solution by partial crystallization. However, the process was time-consuming to lower the Cr^{6+} concentration. It is suggested to use sulfate-based agents to reduce Cr^{6+} to Cr^{3+}. In step III, neutralization treatment for the bulk of F^- using Ca $(OH)_2$, followed by hydroxide precipitation of metal ions (Fe, Ni, and Cr) using NaOH. The resulting filtrate was polished using $ZrOCl_2$ reagent to reduce F^- concentration to 0.12 mg/L. The resultant filtrate was recycled as $NaNO_3$. The adsorption isotherm of the toxic Cr^{6+} ion exchange resin followed the Langmuir model and pseudo-second-order kinetics up to 100 mg/L Cr^{6+} concentration. The presented characteristics of the pickling sludge composition may be useful in overcoming the traditional neutralization problem by removing toxic Cr^{6+}, conversion of nitrate and allowable fluoride discharge, economic aspects of stainless-steel production, and general issues related to environmental pollution and sustainability. This indigenously developed technology can ultimately be tested on a pilot scale basis in batch mode.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
CPCB	Central Pollution Control Board (India)
Cr^{3+}	Trivalent chromium
Cr^{6+}	Hexavalent chromium
DM water	Demineralized water
F^{-}	Total Fluorides
FM	Flame Photometry
MII	Metallurgical Industries of India
$NaNO_3$	Sodium itrate
$Na_2Cr_2O_7$	Sodium dichromate
NO^{3-}	Nitrates
Na^{+}	Sodium ions
PE	Process Flow Sheet
SBA	Strong Base Anion
SE	Synthetic Effluent
TDS	Total dissolved salts
TE	Treated effluent
TSS	Total suspended solids
UF	Ultrafilter
UPS	Used Pickling Solution
UV/VIS	Ultraviolet-Visible Spectrophotometer
$ZrOCl_2$	Zirconyl chloride

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OBRADA LUŽINE IZ PROCESA DEKAPIRANJA NERĐAJUĆEG ČELIKA KUPLOVANE SA NEUTRALIZACIJOM SMOLOM: ISTRAŽIVAČKA STUDIJA

Jedan od najvećih ekoloških problema izazvanih industrijom nerđajućeg čelika su tečni efluenti koji nastaju tokom proizvodnih procesa. Oni sadrže visoku koncentraciju metalnih jona, kao što su Fe(III), Cr(III), Cr(VI) i Ni(II), u smeši HF i HNO_3*, ulja i otpadne vode od ispiranja. Korišćena otpadna lužina iz procesa dekapiranja ima pH od 0,5 i koncentraciju ukupnih rastvorenih soli (TDS) od 520 g/l sa gustinom od 1,20 g/mL. Ovaj rad se fokusirao na reciklažu efluenta za dekapiranje kombinovanjem filtracije, smola i neutralizacije kako bi se efikasno uklonili metalni i fluoridni joni više od 99,5%. Da bi se uklonio TDS, laboratorijski eksperimenti su izvedeni korišćenjem mikro i ultrafiltera sa površinom membrane 0,2* m^2*. Cr(VI) je uklonjen upotrebom TulsionFSMP 6301 smole i desorpcijom korišćenjem* $NaNO_3$ *i naknadnom konverzijom u* $Na_2Cr_2O_7$ *kao nusproizvoda.* $Ca(OH)_2$ *i NaOH korišćeni su za neutralizaciju i taloženje metalnih jona, a dobijeni filtrat je poliran korišćenjem* $ZrOCl_2$ *da bi se efektivno uklonili fluoridni joni do 0,12 mg/l. Nitrat je dobijen kao* $NaNO_3$*. Iz eksperimentalnih podataka za Cr(VI) korišćene su izotermne i kinetičke studije adsorpcije i razvijen je dijagram toka procesa koji se eventualno može testirati na većoj razmeri.*

Ključne reči: otpadni rastvor za dekapiranje, jonska razmena, ultrafiltracija, precipitacija, industrijska reciklaža, tok procesa.