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Research article

Demonstration of acid and water recovery systems: Applicability and operational challenges in Indian metal finishing SMEs

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ABSTRACT

Diffusion dialysis, acid retardation and nanofiltration plants were acquired from Europe and demonstrated in several Indian metal finishing companies over a three year period. These companies are primarily small and medium enterprises (SMEs). Free acid recovery rate from spent pickling baths using diffusion dialysis and retardation was in the range of 78–86% and 30–70% respectively. With nanofiltration, 80% recovery rate of rinse water was obtained. The demonstrations created awareness among the metal finishing companies to reuse resources (acid/water) from the effluent streams. However, lack of efficient oil separators, reliable chemical analysis and trained personnel as well as high investment cost limit the application of these technologies. Local manufacturing, plant customization and centralized treatment are likely to encourage the uptake of such technologies in the Indian metal finishing sector.

1. Introduction

Metal finishing is a surface treatment process that improves wear and tear resistance, imparts corrosion resistance and improves the aesthetics of metal parts. Various metal finishing techniques like electroplating, painting etc. are used to ensure quality and desired service life of metal components in consumer goods, engineering and construction industries. The electroplating industry in India is composed primarily of small and medium enterprises (SMEs) which are part of the supply chain for automobiles (cars, trucks), 2-wheelers (bicycles, scooters), engineering equipment and consumer goods. There are an estimated 12,000 organized units and around 300,000 small scale units in clusters across India (IITM, n.d). Due to the highly acidic waste streams and the hazardous sludge generated, electroplating is classified by Central Pollution Control Board (CPCB) as one of the major polluting industries (CPCB, n.d). Another key SME sector that employs acid pickling is steel rolling. There are around 1800 small and medium sized steel rolling enterprises across India contributing to nearly 70% of long steel output (bars, sections, industrial products etc.) (Srinivas et al., 2013).

As a first step in the metal finishing process, the component is cleaned to remove oil, scales and other surface impurities. Cleaning involves a series of operations including chemicals degreasing and

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acid pickling. Each cleaning step is followed by single or double water rinse to avoid carryover of chemicals to the next bath. The spent pickling acid and wastewater from all process and rinse baths are collected and treated with lime to precipitate the metals before either evaporating the treated water or discharging it. The dewatered sludge is disposed in hazardous waste landfills.

There are several approaches for the recovery of acids from metal finishing waste streams. These include extraction (Agrawal and Sahu, 2009), spray roasting (Kladnig, 2003; Rögener et al., 2009), ion-exchange (Sheedy and Pajunen, 2012), freeze crystallization (Sartor et al., 2009) and various membrane separation based processes like electrodialysis (Chen et al., 2009), diffusion dialysis (Jeong et al., 2005) and membrane distillation (Tomaszewska et al., 2001). Integrated process schemes such as electrolysis and electrodialysis (Peng et al., 2011), microfiltration, adsorption and ion exchange (Wong et al., 2002) have also been employed. The best available technologies are electrodialysis and diffusion dialysis but spray roasting and ion-exchange are employed extensively for spent acids regeneration on large scale (Regel-Rosocka, 2010). For recovery of rinse water in electroplating operations, reverse osmosis in combination with ultrafiltration (Qin et al., 2004) or nanofiltration (Castelblanque and Salimbeni, 2004) have been used.

Though technologies are available, the practice o f acid and rinse water recovery is not established in Indian SMEs. The SMEs perceive the technologies to be expensive, besides being complex to operate and maintain as technical support from the technology supplier is often limited. They are also not convinced about the technical feasibility of these technologies for their waste streams. At the same time, technology suppliers do not perceive SMEs as a potential market citing lack of technical and financial capacity.

This work demonstrates state-of-the-art technologies for acid and rinse water recovery in Indian metal finishing SMEs. Three technologies viz. diffusion dialysis and retardation (ion-exchange) for acid recovery and nanofiltration for rinse water recovery were demonstrated in different industry clusters. Diffusion dialysis is a membrane separation process based on concentration differences across a non-porous anion exchange membrane that allows acids to permeate but retains dissolved metals. Retardation involves sorption of free acid on the ion-exchange resin followed by desorption of the purified acid with deionized water in a counter-current flow. The recovered acid can be recycled while the metal ions and part of the acid that passes through form the waste stream that is usually neutralized and discharged. Nanofiltration is a pressure driven membrane process that concentrates divalent metal ions, allowing the passage of water that can be reused.

All the three technologies are well established in Europe. Nanofiltration is widely applied in the European metal finishing industry for acid bath regeneration as well as for the reuse of rinsing water. Diffusion dialysis is used for the regeneration of used acids. With the use of a simple pressure-free design and modular structure, it is suitable for application in SMEs as well as large companies. Acid retardation is widely applied in European steel plants for the regeneration of used acid from pickling plants. Due to its modular design and automatic operation mode, it is also applicable in SMEs.

The aim of this work was to (a) evaluate the applicability of diffusion dialysis, acid retardation and nanofiltration for acid/water recovery in Indian metal finishing SMEs (or as a solution for common effluent treatment plants, CETPs) considering climatic conditions, operational stability and economic feasibility and (b) understand the challenges involved in the uptake of such technologies in this sector that will help formulate potential solutions.

2. Methodology

The small-scale demonstration plants (Table 1) were fabricated in Europe. The required pre-treatment systems were procured locally. These included oil separators (Pure Tech India, Trichy and Innovation Filter System P. Ltd., Pirangut) and 20 micron polypropylene pleated cartridge filters (Placon Agencies, Chennai) to remove oil and particulate matter from the waste acid/water stream before feeding to the demonstration plant. Fig. 1 shows the installed systems. The demonstrations were conducted between 2013 and 2016 in different locations across India (Fig. 2).

The installation and commissioning of the demonstration plant at each location was done by the project team. At each location, one or two persons in the host company were trained on plant operation. Analysis of the acids for free acid and metal content was done by titrating the acid solution with 1N sodium hydroxide (NaOH) in 0.5 ml steps until the pH reaches 12. A graph was drawn between the volume of NaOH added and $\Delta pH/\Delta V$ (change in pH/difference in NaOH volume) for each step (Fig. 3). The peak points in the graph show the free acid and metal content present in the solution in NaOH equivalents. The treated rinse water was analysed for conductivity, total dissolved solids (TDS) and pH using in-house portable conductivity/TDS and pH meter. Where analytical facilities were not available with the host company, testing was done in accredited labs in the region. Two workshops were conducted at each location during the demonstration period for metal finishing industries in that region. The first workshop was to introduce the technology to the companies and the second was to share the performance results of demonstration plant.

3. Results and discussion

3.1. Performance of demonstration plants

The results for the demonstrations in terms of acid/water recovery are summarized in Fig. 4.

These are average values over the demonstration period in a specific location that ranged from a week (e.g. nanofiltration at Chennai) to several months (e.g. retardation at Pune).

The recovered acid from retardation was reused in the pickling process. This resulted in reduction of fresh acid consumption by 35–40% in the electroplating unit in Pune. In the rolling unit in Ahmedabad, the used acid was internally recycled for preliminary descaling. The recovered water in nanofiltration was reused in the rinsing tank in the electroplating process in Chennai. The concentrate from the plant, which is obtained after recovering the water from the feed, was rich in electroplating chemicals and has the

Table 1
Demonstration plants specifications.

Technology	Diffusion dialysis	Acid retardation	Nanofiltration
Supplier	Deukum GmbH, Germany	Scanacon AB, Sweden	SIMA-tec GmbH, Germany
Plant details	Pilot plant with Fumatech anion exchange membranes Fumasep FAD PET 75 with 20 m^2 active membrane area; flow range 20–25 L/h	MiniFlex with special anion exchange retardation resin SCANACON 0207-0001; flow range 40–50 L/h	PSta15-2 universal membrane test stand with two 2.5″spiral wound modules Filmtec NF90-2540 with total surface area of 5.2 m^2; permeate flow range 20–100 L/h
Limitations	Max. 50 °C ambient temperature	Max. 50 °C ambient temperature	Max. 50 °C ambient temperature; needs cooling above 40 °C