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Recovery and reuse of Ni(II) from rinsewater of electroplating industries

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ABSTRACT

Discharge of nickel compounds, which may occur in both liquid and solid phases, can cause severe environmental problems. In this work, 'point of source' treatment strategy is followed and reduced the nickel content of rinsewater to about less than 1 mg L^{-1} by ion-exchange method using a packed column involving batch recirculation mode of operation and to recovered Ni(II) content by desorption. The treated water could be recycled for rinsing operation.

The nickel from resin is first precipitated as nickel hydroxide to synthesize positive active material and that was used in Nickel/Metal hydride cell. The performances in terms of electrochemical utilization of nickel hydroxide, specific capacity as a function of discharge current density and cycle life were examined and the nickel hydroxide electrode with 5% $CaCO_3$ addition, having 200 mAh g^{-1} specific capacity, could be subjected to charge/discharge cycles at $C/5$ rate for more than 200 cycles without the capacity fading.

1. Introduction

Many plating and battery industries release heavy metals such as cadmium, lead, chromium and nickel in wastewaters. These heavy metals that find many useful applications in our life are very harmful if discharged into natural water resources and pose a serious health hazard [1–8]. The Ni(II) concentration in wastewater from mine drainage, tableware plating, metal finishing and forging has been reported up to 130 mg L^{-1} [9]. The higher concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g., nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, and skin dermatitis [3]. It is also a known carcinogen [4]. The rinsewater [10], from Nickel plating industries having nickel concentrations of 2–900 mg L^{-1} is known to be one of the major toxic pollutants, which necessitates the development of effective and inexpensive methods to recover heavy metal and purify rinse water in a closed-recycle system for water reuse (to achieve a so-called effluent-free technology). Conventional methods for the removal of Ni(II) from wastewaters include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, activated carbon adsorption, ion-exchange, reverse osmosis, electrodialysis, membrane separation processes, etc. The chemical precipitation [11], is the most cost-effective treatment technology. The possibility to precipitate metals in the form of insoluble compounds, mostly metal hydroxides, in solutions containing complexing agents depends on the complex stability constant and the hydroxide solubility product. Adsorption by activated carbon is widely used for the removal of toxic metal and has been studied extensively. In addition to conventional activated carbons, some low cost waste materials such as coir pith [12], hazelnut shell [13], almond husk [14], are also utilized for preparation of activated carbon and applied for nickel removal. The removal Ni(II) by clays [15,16], was used in the fabrication of common products like wall or floor tiles, where nickel ions remain firmly attached and inertized. Higher cation-exchange capacity and development of surface negative charge on clay particles in contact with water also contribute to this promising performance, despite the lower available specific surface area in comparison with granular activated carbon. These methods have several disadvantages of high operating cost, incomplete removal, low selectivity, high energy consumption, and they generate hazardous solid waste that are difficult to eliminate.

A broad range of biomass types including bacteria, algae, yeast, fungi, activated sludge, anaerobic sludge, digested sludge, peat have been used as biosorbents to remove Ni(II) metals from aqueous solution [17–40]. The nickel ion, compared with other heavy metal ions, was a more recalcitrant pollutant and many metal tolerant micro-algae had a relatively low Ni-binding capacity. The removal of nickel ions from electroplating effluent was far from satisfactory. The biosorption of nickel by different strains of microorganisms was less than that of other metal ions. This was probably due to the intrinsic chemical properties of nickel ions leading to steric hindrance of biosorption. Studies focusing specifically on nickel removal are rare. There is still no satisfactory precedent of employ-

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ing biosorbent in the removal of nickel ions and the feasibility of employing micro-algae to remove Ni from electroplating wastewater is uncertain.

Ion exchange has been widely applied for removal of heavy metal ions from electroplating effluent because it is effective and easy to operate. Recovery and removal of nickel ions from wastewater using ion-exchange method [41–46], was used. However, ion-exchange resins must be regenerated by additive chemical reagents (acid and alkali) when they are saturated and this causes serious secondary pollution. As an alternative technique, electrodialysis is not economical for treating dilute solution because of its high electrical resistance and the development of concentration polarization phenomena. The combination of electrodialysis and ion-exchange methods (electro-deionization) can be applied to the removal of Ni(II) ions [47–55], from diluted solutions. Electrodeionization includes two processes, which are carried out simultaneously: concentration of ions in the ion exchanger (sorption) and transport of ions through the ion exchanger and membrane system caused by a potential gradient and presence of oxidizing impurities in the solution to be purified results in destruction of the resin. The possibilities of electrochemical technology to remove nickel from dilute industrial solutions were reviewed critically [56]. It is inefficient to first deposit nickel and then dissolve. It may be more efficient to make a concentrated solution of nickel using a hybrid ion-exchange/electrodialysis system. Recently, the development of new technologies as alternatives to traditional methods is required to treat wastewaters, the $Mg(OH)_2$-nanotubes/Al_2O_3 composite membranes [57], oxidized multi-wall carbon nanotubes [58], can be reused to remove Ni^{2+} from water repeatedly with still high effectiveness. The superior performances of metal ions removal are preliminary interpreted and are presumably ascribed decisively to the nanostructures.

The objective this paper is to develop an efficient effluent-free technology to reduce the nickel content of rinse water to about less than 1 mg L^{-1} so that the treated water could be recycled for rinsing and subsequently to workout methodology to recover Ni(II) by ion exchange using a packed column involving batch recirculation mode of operation. The recovered Ni(II) from resin could used either for making up the plating bath or alternatively the recovered Ni(II) from the resin could be precipitated as nickel hydroxide to synthesize positive active material that can be used in Nickel/Metal hydride cell.

The active material in the nickel electrode has a theoretical specific capacity 289 mAh g^{-1} according to the equation

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$$

$$E^\circ = 0.395\,\text{VversusHg/HgO} \qquad (1)$$

The performances in terms of electrochemical utilization of nickel hydroxide, specific capacity as a function of discharge current density and cycle life were analyzed and reported.

2. Materials and methods

All the reagents and chemicals used were of analytical grade. For adjusting the pH of the medium 0.1N solutions of NaOH and HCl were used. Based on the practical data collected from different plating industries, the synthetic rinsewater of Ni(II) ion of appropriate concentrations were prepared by diluting the nickel electrolytic plating bath of the following composition: 200 g L^{-1} of $NiSO_4$, 40 g L^{-1} of $NiCl_2$ and 40 g L^{-1} of boric acid in water. The solution prepared in this method resembles the rinsewater that found in the actual rinse tank. All the solutions were made with double distilled water. The Amberlite IR-120 cation-exchange resin (density: 0.8 g mL^{-1}, effective particle size: 0.45–0.6 mm) was used for all the experiments. Before using them, the resins were soaked in double distilled water for 12 h and then they were rinsed several times also with double distilled water.

2.1. Batch mode adsorption equilibrium studies

The adsorption capability of Amberlite IR-120 cation-exchange resin towards Ni(II) ions was investigated using the synthetic rinsewater. Adsorption experiments were carried out at pH values where no chemical precipitation of $Ni(OH)_2$ occurs. Accordingly the initial pH value of 5.8 for rinsewater was fixed for the adsorption of Ni(II) ions on cation-exchange resin. Adsorption of Ni(II) ions of 440 mg L^{-1} was conducted by contacting different weighed amounts of exchange resin (7.8, 4.3, 3.2, 2.6, 2.3, 2, 1.9, 1.8, 1.7, 1.6, 1.5 g) with working volume of 100 mL in 250 mL Erlenmeyer flasks under fixed pre-established conditions. Equilibrium was thoroughly verified for the systems from preliminary experiments performed for different prolonged contact times. The flasks containing the resins were kept in a shaker (with the agitation speed of 160 rpm) at controlled temperature (30 °C) for a period of 12 h. The pH of the slurries was recorded at the start and at the end of each experiment to check for any significant pH drift during the adsorption tests. For the higher resin doses, the marginal drift was noticed in the maintained pH values (within 0.8 units). Once equilibrium was attained, the slurries were filtered and equilibrium concentrations were determined. Nickel analysis was performed using a VARIAN Model SPECTRAA 220, atomic absorption spectrophotometer.

Ni(II) uptake, q_e (mg g^{-1} resin), in equilibrium condition was calculated from $q_e = (C_o - C_e)V/W$, where V is the volume sample (in liters), C_o and C_e are the initial and final equilibrium concentrations (mg L^{-1}) of Ni(II) and W is the amount of resin (in grams).

2.2. Adsorption column breakthrough studies

The experimental arrangement is shown in Fig. 1a and it consists of column of graduated Perspex of 2.25 cm inner diameter and 30 cm height. The Perspex column was equipped with a bottom filtration device to prevent the escape of fine resin beads during processing. In each column test, the ion-exchange resin was first soaked in deionized water for at least 12 h to ensure that the resin was fully swelled prior to use. The column was then loaded with 50 g (15 cm) of the resin. The synthetic rinse water of Ni(II) ion of appropriate concentration was passed downward through the column by a peristaltic pump at a fixed flow rate at the room temperature of (30 °C and initial pH of 5.8). A series of experiments were conducted with various influent concentrations (160 mg L^{-1}, 210 mg L^{-1} and 440 mg L^{-1}) and keeping the column height as 15 cm (50 g). The flow rate of the solution was kept at 20 mL min^{-1}. The samples were collected at certain time intervals and were analyzed for Ni(II) using atomic absorption spectrophotometer (VARIAN Model SPECTRAA 220). The above set experiments were repeated by keeping the flow rate of the solution at 30 mL min^{-1}. The column data obtained are breakthrough curves for analysis.

2.3. Adsorption column batch recirculation mode studies

One possible mode of operation of IX column is that involves the continuous recirculation of the rinse water. Due to this, there is a gradual depletion of the concentration of Ni(II) ion in the reservoir of rinse water. The operation is shown in Fig. 1a to conduct experiments under batch continuous recirculation mode. The effluent was taken in the reservoir, which was allowed to flow from the reservoir and was recirculated through the packed column using a peristaltic pump and back to the reservoir itself. The experi-