Removal of nickel ions from automobile industry wastewater using ion exchange resin: Characterization and parameter optimization

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Abstract. Ion exchange is an effect process for removing of heavy metals from wastewater effluents. In the present study, the sorption of nickel ion (Ni (II)) in effluent from wastewater treatment plant of automobile industry was studied by using D113 ion exchange resin. The static shaking absorption experiments revealed that the process of absorption of Ni (II) was more in line with non-monolayer absorption model of Freundlich that with a maximum absorption capacity of 36.13 mg/g. The column experimental data showed that under the optimum operating conditions which was pH 7.0, temperature 30 °C and 20 mL/min of flow rate it could meet the emission standard (GB25467-2010) of China with 10 h of processing time. Desorption rate of D113 resin could reach above 93.6% by using 0.8% H2SO4 with 5 mL/min of flow rate, and the analysis of FT-IR and SEM proved that –OH was the main functional group of the resin participate in metal binding, which demonstrated that the D113 resin could be considered as an effectively way for the advanced treatment of Ni (II) ions in the effluents of automobile industry wastewaters.

1. Introduction
Automobile industry is one of the rapidest developed industries during the past two decades in China. However, large amount of wastewater is produced and discharged to the environment media. The automobile industry wastewater mainly consists of many heavy metals, such as lead, chromium, zinc and nickel ions [1]. Among these heavy metals, the nickel ion (Ni (II)) is a more recalcitrant pollutant ascribed to its widely applications [2,3]. Generally, physical and chemical processes like the air flotation, acid-base neutralization, coagulation and sedimentation are the most commonly used technologies for the treatment of automobile industry wastewater [4]. The above regular treatment processes have been proved to be able to remove Ni (II) to 5 mg/L, even below the level of 1 mg/L [5]. However, in 2013, Beijing government has set in a strict limit of 0.4 mg/L for nickel discharge in the wastewater, which is much stricter than China national standard (1.0 mg/L, DB 11/307-2013&GB 8978-1996 in China). Therefore, an effective and easy to implement advanced treatment method after the regular treatment is required for Ni (II) removal to comply with the stricter regulation limit.

Adsoption, photo-electrocatalysis, floatation, zerovalent iron and reverse osmosis (RO) are generally used to control the Ni (II) concentration in wastewater treatment [6]. Compared with other processes, ion exchange method has many advantages, such as high absorption efficiency, easy
operation and relatively low cost, which has attracted wide attention [6]. Ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other processes like filtration, distillation, and absorption [7,8]. What is more, ion exchange has been successfully used in a wide range of applications from the recovery of heavy metals from industrial wastes to the separation of rare earths or gas mixtures and advanced treatment of industrial wastewater, as well as separation and purification in the food industry [9,10].

In the present work, an effective ion exchange method for removal of nickel ions in automobile industry wastewater effluents was proposed with regard to the low Ni (II) ions (<1.0 mg/L) as shown. The objectives of this work were: 1) to acquire the absorption properties under different factors in a static absorption experiment; 2) to attain the optimum operating parameters of initial pH, temperature, flow rate in a column experiment; 3) to characterize the resin structure change after absorbed Ni (II) in order to investigate the regeneration properties of D113 resin.

2. Materials and methods

2.1. Materials and chemicals

The exchange resin used in this study was D113 type that purchased from Beijing Huiyuan Co., Ltd. D113 resin was a typical cation exchange resin with carboxylic acid group (-COOH) on macroporous acrylic copolymer (Figure 1). The physical and chemical properties of the D113 resin material were summarized as the bead size of D113 resin ranges from 0.3 to 1.25 mm with a density of 1.15 kg/m³. Other chemicals include hydrochloric acid (HCl, 37%, reagent grade, Scharlau), sodium hydroxide (NaOH, 99%), nickel sulfate heptahydrate (NiSO₄·7H₂O, 99%) and the water was purified in the laboratory by means of a Milli-Q system (Millipore).

![Figure 1. The molecular structure formula of D113 resin.](image1)

![Figure 2. Schematic diagram of column absorption experiment.](image2)

2.2. Collection of wastewater sample

The wastewater samples were systematically collected in high-density polyethylene bottles from effluents of wastewater treatment plant (WWTP) in BAIC Motor Co., Ltd (founded in 2011, Beijing, China; Treatment process: Physical and chemical pre-treatment according to different quality of influents + anaerobic/aerobic biological treatment; Treatment capacity: 2,000 m³/d). The above sampling bottles were immediately transported to the laboratory within 4 h by an ice chamber and then the bottles were preserved in refrigerator at 4 ºC for further analysis.

2.3. Experimental process

The D113 resin was first rinsed by deionized water until the effluents were transparent. Then the D113 resin was soaked in deionized water, 4% HCl and 4% NaOH for 24h respectively before it was dried for 12 h (60 ºC). Finally, the dried resin was soaked in 10% NaCl to prevent dehydration rupture, and washed repeatedly with deionized water. The static absorption test was carried out in 250 mL capacity
flask with resin dosage of 0.2 g. Deionized water and NiSO$_4$·7H$_2$O were configured as 100 mg/L simulated nickel-containing wastewater for static absorption experiments. The pH and temperature are important factors controlling the absorption in the ion exchange process [11,12]. So, the absorption capacity experiment was investigated under different pH value (4 - 9) by using 100 mg/L Ni (II) solutions (100 mL) at 20 - 40 ºC in the orbital shaker (100 rpm) for 4 h, respectively. Afterwards, the nickel containing wastewater with 20, 40, 60, 80 mg/L nickel concentration was also prepared by the method above to investigate the equilibrium absorption and exchange capacity ($q_e$) of different concentration of nickel containing wastewater with 100 mL solution under the same experimental conditions.

In the column experiment, sorption in a continuous-flow system was performed in a fixed – bed glass column with 5.0 cm internal diameter and 45 cm height, packed with 10 cm (200mL) of D113 resin. The wastewater sample which the initial Ni (II) ions concentration was 1.83 mg/L was pumped through column by a peristaltic pump in down-flow mode. The schematic diagram of the fixed – bed plexiglass column reactor was showed in Figure 2. Desorption of Ni (II) ions from the resin was carried out by passing 500mL, 4% (w/w) HCl solution through the column bed in down-flow mode at a flow rate of 10 mL/min. After the completion of desorption, the column was rinsed with deionized water in the same manner as for sorption till the eluting deionized water attained pH 7.0. The desorbed and regenerated column bed was reused for next cycle. All experiments were carried out in duplicates and the deviations were within 5%.

2.4. Apparatus and data analysis
Perkin Elmer model SIMAA 6000 atomic absorption spectrometer (AAS) operating with an air-acetylene flame was used to determine the concentration of Ni (II) in solutions at 231.6 nm. The pH was detected with a handheld pH meter (Shanghai Precision & Scientific Instrument Co., Ltd). A thermostated shaker of orbital model incubator (Gongyi Scientific Instrument Co., Ltd) was used for ion-exchange and temperature experiments. All other analyses were performed in our laboratory according to standard methods of China (MEP, 2002). Infrared spectra of the resins before and after ion-exchange experiment were obtained using a Fourier transform infrared spectrometer in the range of 400-4000 cm$^{-1}$ (Nicolet 5700). Finely ground resins were formed into pellets with IR-grade KBr in the ratio of 1:200 to prepare the translucent sample disks. The surface of ion-exchanger was also characterized by scanning electron microscopy (LED-1450 Scanning Electron Microscopy) before and after the ion-exchange experiments. Samples were gold coated prior to SEM observation.

The Ni (II) sorption capacity ($q_e$) of D113 resin was calculated according to mass balance in Eq. (1), which the $C_0$, $C_i$ was the concentration of Ni (II) at the initial stage and equilibrium of absorption, respectively. Freundlich isothermal equation (Eq. (2)) was used to describe the dynamics of ion exchange processes. Where $n$ and $K_f$ represented empirical constants specific to the system, depending on the working temperature. The equation for the enthalpy of ion exchange absorption of nickel is illustrated in Eq. (3).

$$q_e = \frac{C_0 - C_i}{m} \times V$$

$$\ln q_e - \ln K_f = \ln C_e/n$$

$$\ln \left( \frac{d\epsilon}{\epsilon_c} \right) = -\frac{\Delta H}{RT} + C$$

3. Results and discussion
3.1. Static absorption performance optimization
The changes in the absorption capacity of nickel on the resin under different pH conditions were studied by the above experimental method and the result was shown in the following diagram.
Figure 3 showed that the absorption capacity of the resin was greatly reduced by the effect of the reaction of the reverse ion which explained for the phenomenon that the absorption capacity increases gradually when pH was between 4 and 7. Also, the absorption capacity was basically flat with the amount of absorption was within the range of 34-36 mg/g while the pH was 6 or 7. This is mainly attributed to the special structure of the D113 resin, which the acetate ion would not dissociate lead to a reduce for combination of acetic acid group and nickel ion when the pH was too low, even lower than the value of pKa for acetic acid (COOH⁻). On the contrary, when the solution pH was close to neutral (pH 7), there was a weak absorption competition between hydrogen ions and nickel ions and the former dominates due to the reduction of hydrogen ions. For higher pH which was pH 9, the breakthrough time was the longest for the tendency of ion exchange process to exchange ion with ion that have greater affinity makes sodium ion (Na⁺) was more favourable ion in the process [11,12].

The concentration gradient of nickel ion in water distribution was set to 20, 40, 60, 80 and 100 mg/L to determine the equilibrium concentration of Ni (II) in the solution after absorption exchange as well as the calculation of the equilibrium absorption capacity for the D113 resin. The absorption isotherm curve was shown in Figure 4. At 25 °C of temperature, 4 hours of absorption time, and the initial concentration of nickel solution was 0-100 mg/L, it showed that the absorption capacity of the resin rose with the increase of nickel ion concentration and reached a maximum of 36.13 mg/g within the concentration of 100 mg/L. Then, the absorption isotherms were fitted according to different absorption isotherms in order to reflect the form and extent of resin liquid phase absorption. The linear fitting equation and parameters of the Freundlich model was shown in table 1.

As it can be seen above, the absorption process was consistent with the Freundlich equation as the correlation coefficient attained 0.97. Besides, since the absorption characteristic constant (n) of nickel ion on D113 resin was 1.723 (n>1), which indicated that there is a promoting effect on the absorption process [13]. Fom the Eq.(4), a linear fitting was performed from ln(qe/Ce) to 1/T, and the result of enthalpy change (ΔH) was calculated to be greater than “0” based on the slope of the fitting line,
which suggested the process of D113 resin adsorbed nickel was an endothermic reaction, and within a certain temperature range, higher temperature could promote the absorption process.

3.2. Dynamic absorption performance optimization

The effect of pH and temperature on the sorption of Ni (II) ions was tested under different temperature of 20 °C, 30 °C and 40 °C with 30 mL/min of constant flow for the wastewater sample via the pump. And the residual Ni (II) ions concentration was detected after 60 min from the wastewater flowed out of the absorption column. The effect of pH and temperature on sorption capacity of Ni (II) ions on D113 resin was summarized in Figure 5.

![Figure 5. Effect of pH and temperature on the concentration of nickel ions in effluent (The number of samples analyzed: 4).](image)

As indicated above, the maximum uptake of Ni (II) occurred at initial pH of 6.0 and temperature of 40 °C, and the removal efficiency of Ni (II) ions increased with the increasing of reaction temperature, which was similar to previous research [14]. In view of WWTP of the automotive industry was about 30 °C and the implementation of high temperature conditions will also result in higher costs, as a result, all the following sorption experiments were carried out at pH of 7.0 and temperature of 30 °C.

The effect of flow rate on the sorption of Ni (II) was tested at different flow rate (10-30 mL/min) with different time after the wastewater flowed out of the absorption column was given in Figure 6. As presented above, the Ni (II) of concentrations increased slowly in the initial reaction with a high removal efficiency of Ni (II), and with the flow rate raised, the concentration of nickel ions in the effluent was also increased after the same absorption time which may be attributed to the follow reasons: 1) The increased of flow rate leads to a decrease in the time of nickel ion interaction with the resin surface active groups, then the ion exchange resin penetration time would be shortened so that the resin was not fully utilized; 2) There were other metal ions and organic pollutants in the automobile waste water reacted with the resin in the process of reaction, which affected the absorption capacity of the resin. After 12 h of operation, the resin could still maintain a high removal capacity of Ni (II). Considered the discharge limit of Ni (II) (0.4 mg/L, GB25467-2010, China), the processing parameters of 20 mL/min flow rate and 10 h treated time with the solution pH of 7 was selected as the optimum conditions in the adsorptive operation.

3.3. Regeneration and mechanism

The regeneration of exhausted ion exchange resin was an important factor to minimize the cost of operation. In this research, the regeneration of D113 resin was accomplished by using 0.8% H₂SO₄ as proposed by the manufacturer. The H⁺ in the acid solution will exchanged with the Ni²⁺ in the immobile particle due to the selectively. In this experiment, the 0.8% H₂SO₄ was allowed to flow into the column for 40 min with flow rate of 5 mL/min. The results showed that desorption rate can reach above 93.6%.
In the process of regeneration, the peaks in the spectra was around 3446.7 cm\(^{-1}\) for strong bands of the -OH stretching vibrations were observed for both situations (Figure 7). On the lower frequency side of this band at about 2926.92 cm\(^{-1}\) related to the stretching vibrations of the ring – CH\(_2\) of the resin. In addition, the COO- asymmetric band at 1710.1 cm\(^{-1}\) was shifted to 1567.1 cm\(^{-1}\), which provided evidence that the functional groups of –OH were involved in binding the Ni (II) onto D113 resin. The morphologic characterization of saturated and regenerative D113 resin was shown in Figure 8a and 8b, respectively. As depicted, large number of substances were embedded in the resin channels, and then restored to the form of Na\(^+\) after acid regeneration cycle that it could be used again for nickel removal.

![FT-IR spectra of D113 resin before (1) and after (2) absorbed Ni (II).](image)

![SEM micrographs of D113 resin before (a) and after (b) Ni (II) sorption.](image)

The ion exchanger was regarded as the stationary phase, and the compounds then were separated according to the difference in their surface charges to create the difference of charge-charge interactions between them. The remediation mechanism of ion exchange could be represented as followings (Eq. (4)) [15, 16]:

\[
RA_2^+ + B^{2+} \rightarrow RB + 2A^+ 
\]

Where R was the ion exchange radical and B refers to Ni\(^{2+}\) ions to be removed in this research. Therefore, for the process of absorption in the research, D113 was a cation exchange resin with carboxyl (-COOH) on the large pore structure of acrylic copolymer. The mechanism of removal nickel and regeneration of exchange resin can be described as (RCOO)\(_2\)Ni and metal cations (Na\(^+\)) were generated after nickel ions through the exchange column and reacted with the resin displacement. In addition, the process for the regeneration of exhausted ion exchange resin used sulphuric acid could be described that the H\(^+\) and SO\(_4^{2-}\) ions reacted with (RCOO)\(_2\)Ni to produce RCOOH and NiSO\(_4\) to achieve the purpose of recycling.

4. Conclusion
In this study, the removal of Ni (II) from effluents of WWTP in an automobile industry company was investigated under different experimental conditions such as pH, temperature and flow rate. The static absorption experiments were evaluated with Freundlich isotherms with a maximum absorption capacity of 36.13 mg/g. In addition to higher values of correlation coefficients, monolayer capacities determined from absorption isotherm and intensities, the absorption process of Ni (II) by D113 resin was also determined as non-monolayer absorption. Column tests showed this ion exchange process was pH-dependent and under the optimum conditions of pH 7.0, temperature 30 °C and 20 mL/min flow rate, the experimental device could treat wastewater for 10 h to meet the discharge limits of Ni (II). A high desorption rate of 93.6% was attained using the 0.8% H\(_2\)SO\(_4\) with flow rate of 5 mL/min for D113 resin. And after the SEM and FT-IR study, it was found that –OH was the main functional group of the resin participate in metal binding. The experiments showed that it was possible to apply D113 resin for the advanced treatment of Ni (II) ions in the effluents of automobile industry wastewaters.
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