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Adsorption of Nickel and Chromium Ions by Amine-Functionalized Silica Aerogel

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Abstract. In this study, silica aerogel was synthesized by drying at atmospheric pressure and modified further with aminopropyl triethoxysilane (APTES). The amine-functionalized silica aerogel was investigated as an adsorbent for removal of nickel and chromium ions. The effect of contact time, solution pH, and initial solution concentration were studied. The equilibrium was achieved within 60 min. The optimum pH was found to be 4. Adsorption equilibrium data were agreed fairly well with Langmuir isotherm model. Adsorption capacities for nickel and chromium ions were found to be 40.32 mg/g and 46.08 mg/g, respectively.

1 Introduction

Electroplating is one of the most hazardous chemical industries due to its metal-contaminated wastewater. Heavy metals cause environmental problems as pollutants because of their characteristics such as high toxicity, non-biodegradability, and accumulation in food chain [1]. Therefore, electroplating wastewater must be treated before discharge.

Treating electroplating wastewater can be employed by various techniques such as chemical precipitation, coagulation-flocculation, floatation, adsorption, ion-exchange, membrane filtration, and electrochemical processes. Among them, adsorption is one of the most promising techniques when initial heavy metal concentration below 100 ppm [2]. Adsorption process is simple design, easy to use, and flexible. Moreover, it has low operating cost, low fouling problems, and most economic for elimination of heavy metals from wastewater [3].

Many adsorbents have been developed in treatment of effluent comprising heavy metals. Because of high surface area and porous network, activated carbon has been investigated extensively. However, the adsorption capacity is quite low. This may be caused by lacking of surface affinity groups [4].

Aerogels are interesting material. They have extraordinary characteristics such as high porosity, low density, high specific surface area, with tailor-made surface chemistry [1, 4]. Normally, aerogels are prepared by a sol-gel technique followed by suitable drying methods. To conserve the three-dimensional and the highly porous structure, various procedures are employed such as supercritical drying, freeze drying, and drying at atmospheric pressure. In this study, silica aerogel was synthesized by drying at atmospheric pressure which is easy and safe. Furthermore, modification of adsorbents with some chemicals containing N, O, S, P in functional groups increases adsorption capacity of heavy metals [4]. The objective of this work was to study the adsorption of nickel and chromium from aqueous solutions by amine-functionalized silica aerogel.

2 Materials and methods

2.1. Chemicals

Tetraethylothosilicate (Sigma Aldrich), APTES (Sigma Aldrich), Cetyltrimethylammonium bromide (Fluka), isopropanol (Merck), toluene (Merck), hydrochloric acid (Carlo Erba), and ammonia (Labscan) were used without further purification.

2.2 Preparation and modification of the adsorbent

Silica aerogel was synthesized by a procedure adjusted from that of Aravind et al. [5]. Briefly, 4.66 g Tetraethylothosilicate (TEOS), 5.37 g isopropanol, 6.44 g HCL solution were mixed together. Then, gelation was conducted by adjusting pH to 5 using ammonia solution. The resulted hydrogel was kept at 50°C for 1 day. After that, the pore liquid was replaced with isopropanol. The alcogel was then aged further with TEOS solution. After silylation, replace unreacted TEOS with 0.05% CTAB in isopropanol and dry slowly at 70°C.

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Amine-functionalized silica aerogel was prepared according to Parida and Rath [6]. Briefly, 2.00 g of silica aerogel was mixed with 60 mL toluene and then 1.2 mL of APTES was added drop wise. The mixture was refluxed for 8 hours. The resulted solid was washed with ethanol followed by distilled water. Finally, it was dried at room temperature for 12 hours.

2.3 Adsorption experiments

All adsorption experiments were conducted on a shaker using erlenmayer flasks containing 100 mL of single metal solution and 100 mg of amine-functionalized silica aerogel. The effects of several parameters including contact time, pH, and metal concentration were examined. After filtration of the adsorbent, the metal concentration was measured by UV-visible spectrophotometer. The equilibrium adsorption capacity was calculated by Eq. (1).

$$q_e = (C_0 - C_e)V/m \qquad (1)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_0 is the initial metal concentration (mg/L), C_e is the equilibrium metal concentration (mg/L), V is the solution volume (L), and m is the adsorbent mass (g).

3 Results and discussions

3.1 Properties of silica aerogel

The synthesis of silica aerogel was comprised of 3 steps: (a) sol-gel process (b) aging process (3) drying at atmospheric pressure. Firstly, reactive monomers were generated from hydrolysis of TEOS. Then, three-dimensional open network structure was constructed via condensation reaction. The gel prepared was strengthened by aging process. Finally, the pore liquid was released by drying. During evaporation of the pore liquid, capillary stress occurred leading to mechanical damage. Therefore, drying process was the critical step. TEOS was applied to change gel surface to be hydrophobic. Moreover, the pore liquid was exchanged to isopropanol to lower surface tension. CTAB was utilized to reduce shrinkage and prevent cracking as well. After drying at ambient pressure, silica aerogel synthesized was shown in Figure 1.

Fig. 1. Silica aerogel.

Figure 2 demonstrates the adsorption-desorption isotherm of N_2 at 77 K for silica aerogel. It was found that silica aerogel produced was mesoporous material because of the existence of hysteresis loop. The hysteresis loop was caused by the capillary condensation in the mesopores. The BET surface area of this synthesized material was 1,401.3 m^2/g while the average pore size was 21.2 nm.

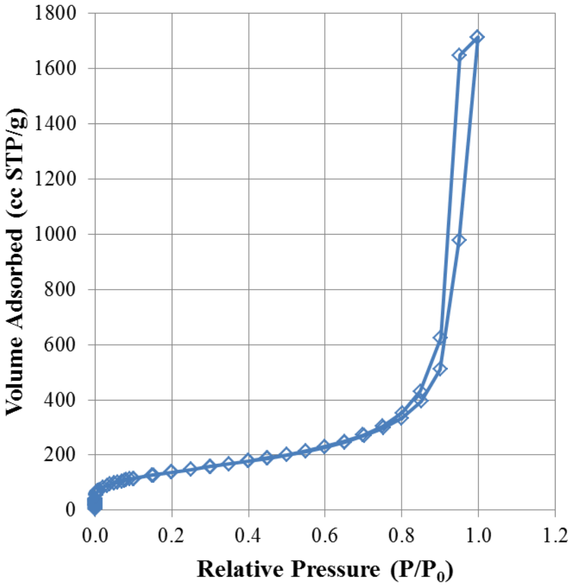

Fig. 2. Adsorption-desorption isotherm of N_2 for silica aerogel.

3.2 Effect of contact time

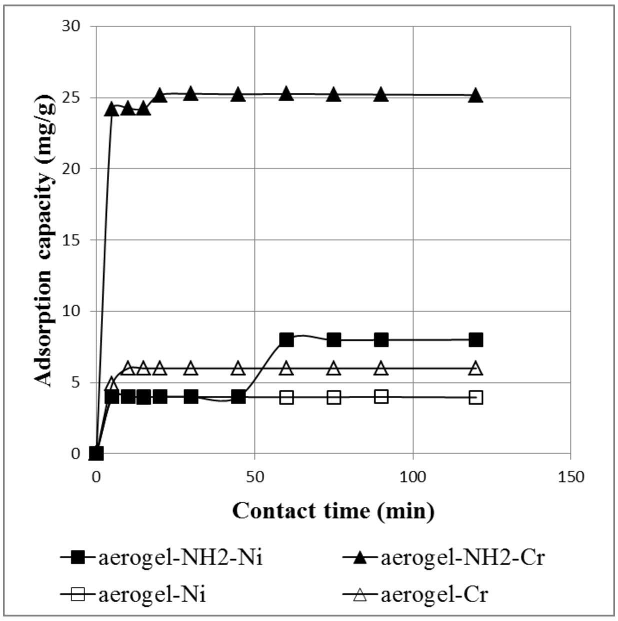

Fig. 3. Contact time effect.

The effect of contact time on the adsorption of nickel and chromium ions was carried out in the range of 0-120 min as illustrated as Figure 3. The adsorption capacity increased dramatically within the first 5 min. Most of them reached equilibrium within 20 min except for the adsorption of nickel by modified silica aerogel. At the beginning of the adsorption process, there were plenty of adsorption sites resulting in high adsorption rate. The contact time of 60 min was selected for all subsequent experiments. In addition, modification of silica aerogel with APTES improved adsorption capacity of both nickel and chromium ions. The amino groups on the adsorbent surface can form a coordination complex with metal ion [4].

3.3 Effect of pH

One important factor governing adsorption process is the solution pH. The effect of the solution pH on the removal of nickel and chromium ions was investigated at pH 1-4 and the result are presented in Figure 4. It was found that the increase of solution pH resulted in the increase of adsorption capacity. This may be caused by competition between hydrogen ions and metal ions at low pH [1].

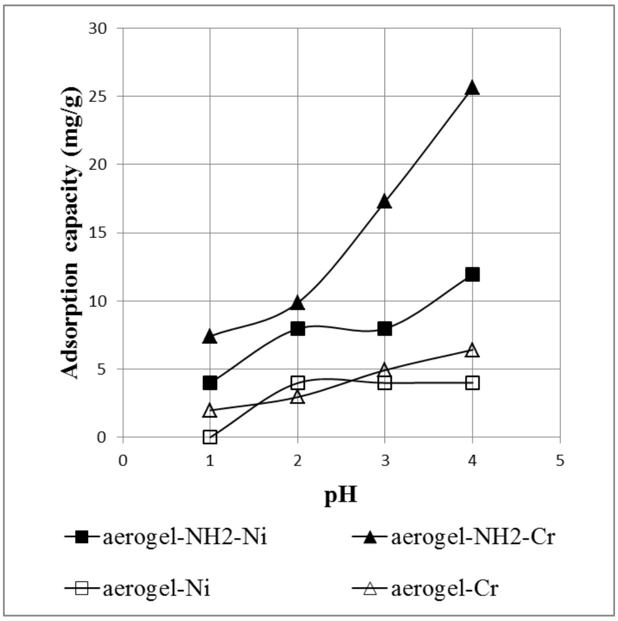

Fig. 4. The effect of pH.

3.4 Adsorption isotherm

As shown in Figure 5, adsorption capacity increased when metal concentration increased due to higher driving force of the metal ions. This figure also indicates that adsorption capacity of chromium ion was higher than that of nickel. This was caused by higher charge to radius ratio (Z/r) of chromium ion [4].

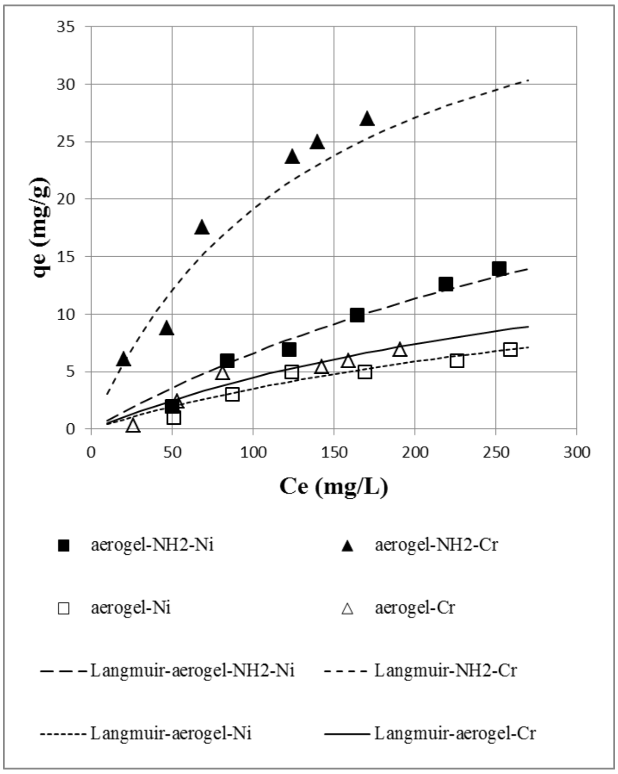

Fig. 5. Metal concentration effect and adsorption isotherm.

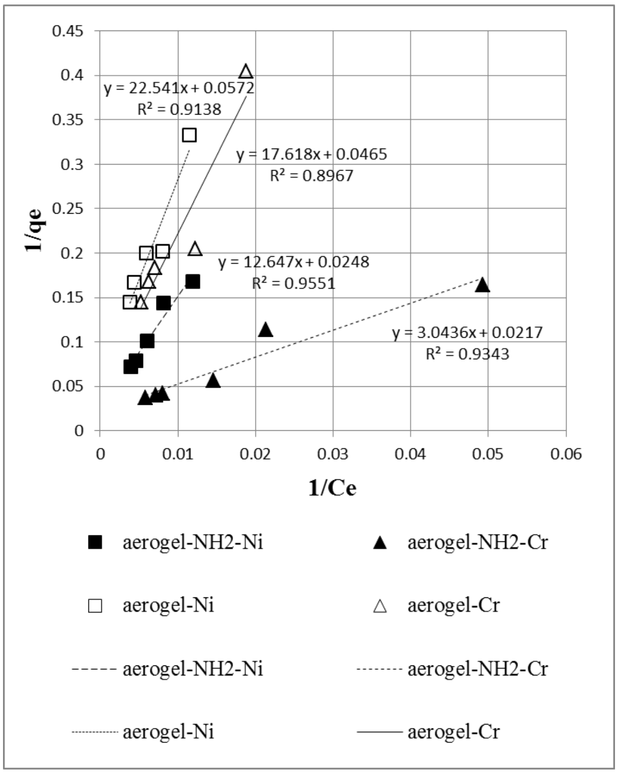

Fig. 6. The linear Langmuir model.

To design any sorption system, adsorption isotherms are the important information. In this study Langmuir isotherm was chosen. It can be shown by equation (2):

$$q_e = Q_m b C_e/(1+bC_e) \qquad (2)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium metal concentration (mg/L), Q_m is the maximum adsorption capacity (mg/g), b is the equilibrium constant (L/mg). To obtain the model parameters, the linearized Langmuir equation was used as equation (3):

$$1/q_e = (1/Q_m b)(1/C_e) + (1/Q_m) \quad (3)$$

Linear Langmuir plot is displayed in Figure 6 and the obtained isotherm parameters are summarized in Table 1. It can be seen in Figure 5 that the Langmuir isotherm fitted the experimental data fairly well. The maximum adsorption capacities for nickel and chromium ions on amine-functionalized silica aerogel were found to be 40.32 mg/g and 46.08 mg/g, respectively.

Table 1. Isotherm parameters.

Adsorbent/adsorbate	Q_m **(mg/g)**	***b*** **(L/mg)**	R^2
Aerogel/Ni	17.48	0.0025	0.914
Aerogel/Cr	21.51	0.0026	0.897
Amine-aerogel/Ni	40.32	0.0020	0.955
Amine-aerogel/Cr	46.08	0.0071	0.934

4 Conclusions

Adsorption of nickel and chromium ions onto amine-functionalized silica aerogel was studied. It was found that adsorption process achieved equilibrium within 60 min. The removal of both metals was optimum at pH 4. The adsorption loading of chromium ion was higher than that of nickel ion. The Langmuir model fitted the experimental data fairly well.

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