Comparision of Low-Cost and Eco-Friendly Adsorbent for Adsorption of Ni(II)

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INTRODUCTION

Arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), and nickel (Ni) are heavy metals and of great concern. They are not biodegradable, tend to accumulate in living organisms, and cause various diseases and disorders (1). Chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and adsorption are some of the methods used for removal of these and other metals. The process of adsorption has become one of the preferred methods for removal of toxic contaminants because the adsorption method is very effective, economical, versatile, and simple. Additional advantages are its applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, and the possibility of regeneration and reuse (2). Different solid phases have been used as solid-phase extractants for enrichment of trace metal ions (3). In the past two decades, researchers have mostly been using low-cost effective adsorbents for heavy metal adsorption, and the sorption behavior of several natural waste materials have also been investigated (1). Numerous adsorbents, obtained from natural wastes have been used for the removal of aluminum, nickel, cadmium, chromium, copper, iron, lead, and zinc and include the leaf, stem, and root phytomass of holly oak (4), CACMM2 powder extracted from a cactus (5), starch, activated charcoal, wood charcoal, and clay (6), groundnut husks (7), bark (8-10),

ABSTRACT

In this study, samples of clay, tea waste, astragalus plant, chestnut shell, and egg shell were used as low-cost and eco-friendly adsorbents for the adsorption of Ni(II) from aqueous solutions. The effect of various parameters such as pH, contact time, adsorbent dose, and final volume on the adsorption capacities of these natural adsorbents were investigated by batch experiments. The adsorption capacity for Ni(II) was found to be 19.4 mg g⁻¹, 5.4 mg g⁻¹, 1.3 mg g⁻¹, 5.6 mg g⁻¹, 72.0 mg g⁻¹ for clay, tea waste, astragalus plant, chestnut shell, and egg shell, respectively. Egg shell has maximum adsorption capacity at pH 12, 45-minute contact time, and 0.5 g adsorbent mass. Nickel-free and nickel-loaded adsorbents were characterized by FTIR spectroscopy, which evidenced the functional groups involved in nickel uptake. This work investigated the utilization of eco-friendly and low-cost adsorbents as an alternative natural adsorbent for Ni(II) ions.

sunflower stalks (11), bagasse (12), rice husk (13) and sawdust (14,15).

Atomic spectrometry techniques are generally used for the quantification of metals. Flame atomic absorption spectrometry (FAAS) has advantages such as low cost, good selectivity, and high analytical frequency. However, the direct determination of trace metals by this technique can be difficult because of the low concentration of these metals in the samples (16). Sample solutions with low concentrations require a preconcentration method. Solid phase extraction is a simple and eco-friendly procedure

with a high preconcentration factor (17). Column or batch techniques can be used for solid phase extraction. In the batch technique, aqueous samples are added to a suitable vessel containing a sorbent and stirred for a known period of time to attain the sorption equilibrium as quickly as possible. Then the solid phase is separated from the solution by filtration or decantation and the metal ions retained on the sorbent are eluted with a small volume of organic or inorganic solvent. Metals ions are determined in the elution solution by an appropriate analytical technique such as atomic absorption, atomic emission, or mass spectrometry (18). The obvious advantage of the adsorption method is the low costs involved. Hence, there is a need to search for more economical and effective sorbents (19). The objective of this study was to investigate the possibility of using eco-friendly and low cost materials such as clay, tea waste, astragalus plant, chestnut shell, and egg shell, and to compare and evaluate the adsorption capacities of these adsorbents for Ni(II) determination.

EXPERIMENTAL

Chemicals

Analytical grade nickel chloride, sodium hydroxide, hydrochloric acid, sodium citrate monohydrate, sodium dihydrogen phosphate, sodium tetraborate, glycine and nitric acid were used (Merck, Darmstadt, Germany).

Preparation of Natural Adsorbents: Egg Shell, Chestnut, Black Tea, Clay, and Astragalus

The egg shells were washed with distilled water, then calcined in an ashing oven at 900 °C for eight hours. The calcined egg shells

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were ground in a blender and sifted through a <120 mesh sieve.

The chestnuts were purchased at a local market and washed with distilled water to remove any dirt. The samples were cooked on a portable electric heating element, then the skin was peeled off.

The black tea samples were steeped and the residue washed with hot distilled water until the water became colorless. The black tea waste was dried in oven at 60 °C until constant weight.

The clay sample was crushed and milled, washed with distilled water and dried in an oven at 60 °C until constant weight.

The Astragalus plant samples were picked at Tunceli, washed with tap water, then with distilled water. After washing, the samples were dried in an oven at 60 °C until constant weight.

All of the dried adsorbents were ground in a blender, sieved to a particle size of <120 mesh, and stored in polyethylene bags at room temperature until use.

Adsorption Studies

Instrumentation

In this investigation, batch adsorption experiments were performed to determine the adsorption capacities of the chestnut shell, tea waste, astragalus, clay, and egg shell. Batch experiments were carried out at room temperature (25±1 °C) using a magnetic stirrer (Daihan Scientific, MSH-20A, Seoul-Korea) in a Pyrex® beaker covered with stretch film to prevent contamination. The batch adsorption experiments were carried out by shaking a known amount of the natural adsorbent at various pH values, stirring times, adsorbent amounts, and final volumes for the determination of Ni(II) at optimum conditions. The final solutions were filtered through a Macherey-Nagel

640 de 110-mm filter paper (Macherey-Nagel, Düren, Germany), and the remaining Ni concentrations were determined using a PerkinElmer® AAnalyst™ 800 flame atomic absorption spectrometer (FAAS) (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating conditions are listed in Table I.

All experiments were performed in triplicate and the results given here are the average of these measurements. Blank experiments were processed without addition of adsorbents. For the pH adjustments, 0.1M hydrochloric acid and sodium hydroxide were used. A digital Jenco 6173 pH meter (Shanghai Jenco Electronics, Shanghai, China) was used for the pH measurements.

Characterization of Adsorbents

FTIR Spectra for Comparison

Fourier transform infrared (FTIR) spectra of all of the pretreated samples were compared to the FTIR spectra of nickel-loaded clay, tea waste, astragalus plant, chestnut shell, and egg shell. The spectra were recorded in the frequency range of 4000–500 cm⁻¹ using an FTIR spectrophotometer (Thermo Scientific, USA). The samples were crushed and prepared with KBr-forming pellets.

RESULTS AND DISCUSSION

Effect of pH

For pH optimization, 0.25 g of each adsorbent was weighed with a Radwag AS 220/C/2 analytical balance (Radwag Balances & Scales, Poland) and mixed with 50 mL of aqueous Ni(II) solution as follows: astragalus plant, tea waste, chestnut shell with 15.0 mg L⁻¹, clay adsorbent with 100 mg L⁻¹, and egg shell with 360 mg L⁻¹, and then placed in a magnetic stirrer (10–180 minutes). The pH was optimized for citrate from 2–5, phosphate from 6–7,

TABLE I
Instrumental Operating Conditions of AAnalyst 800 FAAS

Parameters	Values
Wavelength	232 nm
HCL current	20.0 mA
Flow rates:	
Air	17 L/min
Acetylene	2 L/min
Slit width	0.2 nm

borate from 8–10, and glycine buffers from 11–13. It was observed that adsorption of Ni(II) was maximum for clay at pH 10, tea waste at pH 9, astragalus plant at pH 7, chestnut shell at pH 7, and egg shell at pH 12. The results are shown in Figure 1 (a and b). The correlation between the metal uptake and pH is related to the acid-base properties of the various functional groups on the adsorbent surfaces, mainly the carboxyl groups (20). The increase in both the metal adsorption and the pH values can be explained as the competition between the proton and nickel ions for the same functional groups and by a decrease in the positive surface charges which results in a higher electrostatic attraction between the surface and the metal (20).

Carvalho et al. (21) obtained different results for clay and tea waste and used the silylated clays to remove Ni(II) from the aqueous effluents. They determined that the maximum value of metal retention occurred at a pH of about 6.0, and that there was a decrease in the capacity of retention in solutions with a reduced pH (21). In another study, tea waste was used as the adsorbent and maximum adsorption of the Ni(II) ions was observed at pH 4.0 (22). Jiang et al. (23) found that the adsorption of Ni(II) increased in kaolinite clay with a pH from 2.0 to 8.0. When the pH increased from 7 to 12,

a significant increase in adsorption (about 6-fold) was observed for egg shell, while for clay it was about 4-fold. There was no big change due to the other parameters such as stirring time, final volume, and adsorbent amount.

Effect of Stirring Time

The influence of contact time on the adsorption of Ni(II) on tea waste, astragalus plant, chestnut shell, and egg shell was evaluated from 10–180 minutes (Figure 2 a and b). The contact time was fixed at 45 minutes for clay, tea waste, and egg shell, at 60 minutes for astragalus plant, and at 90 minutes for chestnut shell. Gupta et al. (24) used waste rubber tire as the adsorbent. In that study, the adsorption efficiency increased to 120 minutes of contact time after which the capacity levelled off. Therefore, they selected 120 minutes as the optimum contact time (24). In the study by Jiang et al., the initial

adsorption was found to be very fast with maximum uptake within 30 minutes for Ni(II) (23).

Effect of Final Volume

The final volume of the Ni solution was studied in addition to the other optimum conditions in order to determine the amount of volume for optimum adsorption. For this purpose, the adsorbents were interacted with Ni(II) solutions which were at the same concentrations (for clay 100 mg L⁻¹, for egg shell 360 mg L⁻¹, for astragalus plant, tea waste and chestnut shell 15 mg L⁻¹) but at different volume (25–400 mL). Figure 3 shows the optimum final volume used for Ni(II) adsorption. According to the obtained results, the solution volume has little effect on the adsorption capacity of the adsorbents. The adsorption capacities were about the same regardless of the volume amount. The final volume selected was 50 mL each for clay, astragalus

plant and egg shell, and 100 mL each for tea waste and chestnut shell.

Effect of Adsorbent Amount

The adsorption of nickel ions on clay, tea waste, astragalus plant, chestnut shell, and egg shell was studied on amounts ranging from 0.1 to 1.0 g in a 50-mL solution volume with a specific stirring time and pH. The adsorbed Ni amount increased with an increase in the adsorbent from 0.1 g to 0.25 g, and decreased after 0.25 g of adsorbent for clay and the astragalus plant. The adsorbed Ni amount increased with an increase in the adsorbent from 0.1 g to 0.5 g and decreased after 0.5 g of adsorbent for tea waste, egg shell, and chestnut shell. Therefore, 0.25 g each of clay and astragalus and 0.5 g each of tea waste, egg shell, and chestnut shell were selected as the adsorbent mass. The adsorption efficiency of

Fig. 1 (a and b). Effect of pH on adsorption capacity of nickel on (a) ♦ clay and ■ egg shell; (b) * astragalus plant, ● tea waste, and ▲ chestnut shell.

Fig. 2 (a and b). Effect of stirring time on adsorption capacity of nickel on (a) ♦ clay and ■ egg shell; (b) * astragalus plant, ● tea waste, and ▲ chestnut shell.

Ni(II) as a function of adsorbent amount is shown in Figure 4.

The decrease in q_e with an increase in the adsorbent amount is mainly due to the unsaturation of the adsorption sites through the adsorption reaction. Another reason may be due to the particle interactions, such as aggregation, resulting from high sorbent concentrations. Such aggregation would lead to a decrease in the total surface area of the adsorbent (25).

Choksi and Joshi (26) investigated the removal of Ni(II) from wastewater using natural adsorbents such as starch, activated charcoal, wood charcoal, and clay. For clay, they determined that the amount adsorbed increased from 0.09 to 0.099 g per 0.25 g of adsorbent with an increase in pH from 6 to 8.5, respectively. For clay, the amount adsorbed increased from 0.098 g per 0.2 g to 0.099 g per

1.0 g at 30 °C, at pH 7.5 for Ni(II).

Ni(II) Adsorption Capacities of Natural Adsorbents

The amount of Ni(II) adsorption was calculated according to the following equation:

$$q_e = (C_0 - C_e) \times V / m \quad \text{Eq. 1}$$

where q_e is the amount (mg g^{-1}) of Ni(II) adsorbed by the clay, tea waste, astragalus plant, chestnut shell, and egg shell adsorbents. C_0 and C_e are the metal concentrations (mg L^{-1}) in the solution initially and after adsorption, respectively. V is the volume (L) of the solution and m is the mass (g) of adsorbent used.

The adsorption percentage was calculated according to the following equation:

$$\text{A\%} = (\text{Amount of adsorbed metal ions} / \text{amount of initial metal ions}) \times 100 \quad \text{Eq. 2}$$

where Ni(II) adsorption capacities of the natural adsorbents were calculated at optimum conditions for each other. The q_e values found were 19.42 mg g^{-1} , 5.44 mg g^{-1} , 1.3 mg g^{-1} , 5.6 mg g^{-1} , and 72 mg g^{-1} for clay, tea waste, astragalus plant, chestnut shell, and egg shell, respectively. According to the obtained results, egg shell has maximum absorption capacity when compared to the other natural eco-friendly adsorbents of this study, and the adsorption capacity of clay was approximately the same. The adsorption percentages were determined as 97.0%, 36.3%, 8.7%, 37.3%, and 99.8% for clay, tea waste, astragalus plant, chestnut shell, and egg shell, respectively.

FTIR Analysis of Adsorbents

The spectra of the adsorbents were measured using a Thermo Nicolet Is10 FT-IR (Thermo Scientific, USA) for the determination of

Fig. 3 (a and b). Effect of final volume on adsorption capacity of nickel on (a) ♦ clay and ■ egg shell; (b) * astragalus plant, ● tea waste, and ▲ chestnut shell.

Fig. 4 (a and b). Effect of adsorbent dose on adsorption capacity of nickel on (a) ♦ clay and ■ egg shell; (b) * astragalus plant, ● tea waste, and ▲ chestnut shell.

the vibrational frequency changes in the functional groups of the adsorbents before and after adsorption of nickel. The FTIR instrumental operating conditions are listed in Table II. Figures 5-9 (a and b) show the peaks of the different adsorbents before and after use.

The adsorption band at approximately 3300 cm^{-1} is attributable to the hydroxyl groups from the polyphenols originally present in the chestnut shell, tea waste, and astragalus plant (Figure 7-9). The peaks observed at 2900 cm^{-1} can be assigned to stretching vibrations of the C-H groups for the chestnut shell, tea waste, and astragalus plant (Figure 7-9) (27). The observed band around 2851 cm^{-1} was assigned to the stretching vibration of the C-H alkane groups for tea waste (28). The band around 1730 cm^{-1} is due to a C=O group of carboxylic acid or its ester for chestnut shell and tea waste (29). The peak around 1620 cm^{-1} is due to the C=C aromatic or may be the asymmetric and symmetric stretching C=O vibration for tea waste (30). The observed band at 1236 cm^{-1} is due to the -SO_3 stretching for chestnut shell, tea waste, and the astragalus plant (29). The bands at $3639\text{-}3617\text{ cm}^{-1}$ for clay and egg shell (Figure 5-6) can be attributed to the hydroxyl groups on the surface material (31). The band at 3407 cm^{-1} can be attributed to the presence of the O-H and N-H groups, while the band at 1634 cm^{-1} reflects the carbonyl group stretching (amide) for clay. The band around 1456 cm^{-1} for clay and egg shell is attributed to the symmetric bending of CH_3 . All of these functions are likely to participate in Ni^{2+} binding to these adsorbents. The shifts and intensity changes of the FTIR bands observed were rather weak, which can be an indication of the dominance of ion exchange over the precipitation/ coprecipitation

TABLE II
Instrumental Parameters
for FTIR Analysis

Wavelength range	$4000\text{-}500\text{ cm}^{-1}$
Sample to KBr mass ratio	1:100
Spectral resolution	4 cm^{-1}

occurring during Ni^{2+} sorption on these sorbents (29).

CONCLUSION

In the present study, a batch technique for the adsorption of Ni(II) has been carried out using clay, tea waste, astragalus plant, chestnut shell, and egg shell as adsorbents and basic procedures are provided for their use. The important parameters for the batch technique such as pH, contact time, adsorbent dose, and final volume were studied for determining their adsorption capacities. It was found that clay and especially egg shell are good adsorbents for Ni(II), and the adsorption percentages are very high. Most of these adsorbents are waste materials, except for clay and the astragalus plant, and all can easily be obtained, are eco-friendly, and low cost.

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Fig. 5 (a and b). FTIR spectra of (a) clay and (b) Ni-loaded clay.

Fig. 6 (a and b). FTIR spectra of (a) egg shell and (b) Ni loaded egg shell.

Fig. 7 (a and b). FTIR spectra of (a) astragalus and (b) Ni-loaded astragalus.

Fig. 8 (a and b). FTIR spectra of (a) tea waste and (b)-Ni loaded tea waste.

Fig. 9 (a and b). FTIR spectra of (a) chestnut shell and (b) Ni-loaded chestnut shell.

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