

A new sand adsorbent for the removal and reuse of nickel ions from aqueous solutions

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ABSTRACT

Nickel ions (Ni(II)) in aqueous solutions were removed by a sand adsorbent with a surface functionalized porous coating. The sand adsorbent has a very large surface area of 150 m²/g. The influence of pH, initial concentration of the solution, temperature, contact time and adsorbent dosage on the removal efficiency of the synthesized sand adsorbent toward Ni(II) in the aqueous solutions were studied. The results indicate that the adsorption of nickel onto the sand adsorbent greatly increases the pH range of 2–4 and slightly increases with temperature from 25 to 40 °C. The maximum removal efficiency and ion retention in per unit mass of the adsorbent were 100% and 5.78 mg/g, respectively, under the specified experimental conditions. The adsorption can be described by the pseudo-second-order kinetic model and the Freundlich adsorption model. The adsorbed nickel (4.24 mg/g) together with the spent adsorbent were successfully employed to prepare a brown glass, suggesting a new way to reutilize the recovered nickel from wastewater and to avoid secondary pollution caused by the used adsorbents.

Key words | adsorbent, adsorption, nickel ion, reutilization, silica sand

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INTRODUCTION

Nickel ions (Ni(II)) are among the toxic heavy metal ions in wastewater that cause serious environmental problems and do harm to the health of people (Fargasova 2012). Many methods have been developed for the purification of the Ni-polluted wastewater. Compared with other methods, the adsorption of Ni(II) from wastewater using adsorbents is simple, efficient and economic. Different types of adsorbents have been synthesized and used for the removal of Ni(II) from synthetic or industrial wastewater. Amino modified SiO₂-based adsorbents were shown to be effective for removing Ni(II) from aqueous solutions (Heidari *et al.* 2009; Hao & Hou 2013). Natural minerals as adsorbents are advantageous over synthetic ones due to their low cost and local availability. However, to improve their performance, modifications might be required. Iakovleva *et al.* (2015) proved that limestone modified with NaCl or mining processing wastewater could purify wastewater containing Ni(II). The efficiency of modified adsorbents was four times higher than an unmodified one. Yadav *et al.* (2013) simply soaked riverbed sand in 40% H₂SO₄ for 4 h and used the modified sand for the treatment of Ni(II) from aqueous solutions with varied initial ion concentrations

under the conditions of pH = 4.0–8.0 and an adsorbent dosage of 1.0–2.0 g. They showed that the removal efficiency decreased from 68.76 to 54.09% when the concentration of Ni(II) was increased from 5 to 15 mg/L. Removal was found to be highly pH dependent, and the maximum removal was achieved at a pH of 8.0. The removal process was exothermic, and followed the first-order kinetics. Boujelben *et al.* (2009) first proved that natural iron oxide-coated sand extracted from an iron ore located in the north-west of Tunisia had a maximum nickel ion retention of 1 mg/g, and followed the Langmuir adsorption model. The same group also reported that modification of the sand by employing iron oxide and manganese oxide coated sand (ICS and MCS) improved the nickel adsorption. The maximum sorption capacities were 2.73 and 3.33 mg Ni/g ICS and MCS, respectively. The nickel uptake process followed the pseudo-second-order rate expression (Boujelben *et al.* 2010).

The regeneration of spent adsorbents has been considered by many researchers (Lata *et al.* 2015). For example, EDTA and 1 M HCl solutions were used to strip off the adsorbed Ni(II) in the afore-mentioned phosphorylated

cellulose triacetate/silica and phosphine-functionalized PVA/SiO₂ composite adsorbents (Islam *et al.* 2015; Srivastava *et al.* 2016). However, reuse cases for the recovered Ni have been seldom reported. We found one example in the literature showing that the recovered nickel in resin was first desorbed with HCl solution, followed by precipitation to form nickel hydroxide, which was further successfully used to synthesize electrode material in a nickel/metal hydride cell (Priya *et al.* 2009).

In this work, targeted at the reutilization of the spent adsorbent with the adsorbed nickel, a new sand adsorbent was synthesized. Briefly, sand used for glass production was first coated with a layer of porous silica, which was further functionalized with aminopropyltriethoxysilane (APTES). Due to the surface coating and functionalization, the sand gained significantly enhanced capability toward adsorption of Ni(II) from aqueous solutions. In the meantime, the nature of the sand as a glass ingredient (Burciard 1905) was not greatly influenced, facilitating the reutilization of the spent sand in colored glass preparation.

EXPERIMENTAL SECTION

The original sand was taken from a glass factory. Other reagents were of analytic grade. The preparation of the sand adsorbent mainly comprised two steps: a surface coating followed by an amino-functionalization. The details were as follows. Briefly, 6.0 g of silica sand, 1.08 g of hexadecyltrimethyl ammonium bromide (CTAB) and 100 ml of distilled water were mixed under shaking in a water bath at 60 °C for 10 min. In this mixture, 30 ml of NaOH solution (0.3 mol/L) and tetraethyl orthosilicate (TEOS) were sequentially added. After reacting for 3 h, the resultant product was carefully washed and filtrated. The collected sample was dried at 90 °C. Afterwards, the surface coating procedures were repeated five times. The final product was calcined at 550 °C for 6 h to remove the organic template, forming a nanoporous silica coated silica sand. For the amino-functionalization of the nanopores (Araghi *et al.* 2015), 5.0 g of porous silica coated sand was mixed with 100 ml of anhydrous toluene under stirring in a three-necked flask. The mixture was heated in an oil bath to 115 °C. Then, 3 ml of APTES was added. After refluxing for 9 h, the solid was collected by filtration, followed by washing with toluene and methanol. The dried sample was collected for the following adsorption tests.

NiSO₄·6H₂O was used to prepare Ni(II) solutions with different concentrations. In 50 ml of the solution, the prepared sand was added as the adsorbent. The influence of

pH, initial Ni(II) concentration (C_0), temperature (T), contact time (t), and adsorbent dosage (m) on the removal efficiency of the synthesized adsorbent toward Ni(II) in the aqueous solutions were studied. The Ni(II) adsorption experiments were performed by adding the sand adsorbent into the Ni(II) solutions in glass beakers, which were under shaking for a period of time in a water bath kept at a particular temperature.

To check the feasibility of using the spent sand adsorbent for the colored glass preparation, the adsorption of Ni(II) was performed in 50 ml solution under the conditions of pH = 6, $C_0 = 50$ mg/L, $m = 0.5$ g, $T = 25$ °C and $t = 6$ h. The spent adsorbent was collected to prepare a glass with a composition of Na₂O 22, CaO 12, SiO₂ 60, MgO 4, and Al₂O₃ 2 by weight percentages. The SiO₂ component was supplied by the spent adsorbent. To get enough SiO₂, parallel adsorption tests were conducted. Apart from SiO₂, the other components in the glass were introduced by chemical reagents. Following the general procedures for glass preparation, the batch containing the necessary fluxing and refining agents was melted in a resistance furnace at 1,350 °C for 2 h. The melt was formed and annealed. After the samples were cooled down to room temperature, they were cut and polished for the visible light transmission spectrum measurement.

The point of zero charge of the original and modified sands was determined by measuring the initial and the final pH of a 50 mL solution of 0.01 M sodium chloride containing adsorbent. The plot between the initial and the final pH of the solution intersected at a point indicating the zero charge of the adsorbents (Chaudhry *et al.* 2016). The optical, scanning and transmission microscope images of the synthesized sand particles were taken on a B1-223A (Motic, China) microscope, QUANTA-250-FEG (FEI, USA) scanning electronic microscope (SEM) and EM1200 EX (JEOL, Japan) transmission electronic microscope (TEM), respectively. The surface area of the sample was determined using N₂-sorption data in an appropriate relative pressure region according to the Brunauer–Emmett–Teller (BET) model (Rouquerol *et al.* 1999). The measurements were performed at 77 K on an ASiQ-C instrument (Quantachrome, USA). The concentrations of the Ni(II) solutions were measured on a PinAAcle900T (PerkinElmer, USA) atomic adsorption spectrometer. The removal efficiencies of the developed sand adsorbent were evaluated based on the initial and final ion concentrations of the solutions. The adsorption capacity was expressed as the retention of nickel ions on a per unit mass of adsorbent (abbreviated as *ion retention* in the

following context). The calculation formulas are as follows:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$\text{Ion retention (mg/g)} = \frac{(C_0 - C_e) \times 50}{1000m}$$

where C_0 and C_e are the initial and equilibrium adsorption concentrations of the ions, and m is the amount of adsorbent, respectively.

The light transmission spectrum of the prepared glass was recorded on a 722 spectrometer (Jinghua, China) over the visible light range.

RESULTS AND DISCUSSION

The characterization of the sand adsorbents

The optical microscope, SEM and TEM images of the synthesized sand adsorbent are shown in Figure 1. It

can be seen from Figure 1(a) that the particles are sized *ca.* 200–400 microns. The hydrolysis and condensation of TEOS led to the formation of the surface coating. The surface of the adsorbent is rough, with some visible cracks (Figure 1(b)) which were probably caused by the contraction of the gel during the drying process. The amplified image suggests that the surface coating consists of micrometer-sized particles along with the gel (Figure 1(c)). The TEM image reveals a partially ordered porous texture of the surface coating (Figure 1(d)). The N_2 -sorption result indicates that the parent sand and the synthesized sand adsorbent have BET surface areas of 0.09 and 150 m^2/g , respectively. To our knowledge, the obtained sand adsorbent has the largest surface area of the reported coated or modified sands used in wastewater purification (Hu *et al.* 2004; Jerez *et al.* 2006). The points of zero charge were found at pH of 6.9 and 8.6 for the original sand and prepared sand adsorbent, respectively. The increase in the pH of the zero charge point identifies the functionalization of the porous silica coated sand by the amino groups, which are protonated in solution.

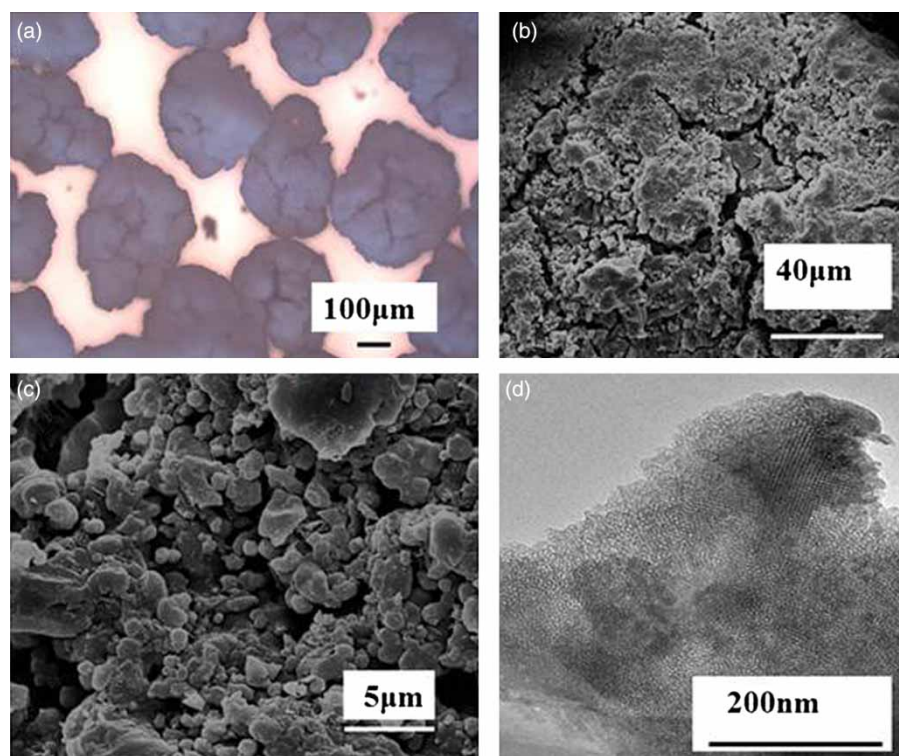


Figure 1 | Optical microscope (a), SEM (b) and (c) and TEM (d) images of the synthesized sand adsorbent.

Factors influencing the adsorption of Ni(II)

Effect of pH

Figure 2 illustrates the pH dependent removal efficiencies and ion retentions of the adsorbent toward Ni(II) under the conditions of $C_0 = 50$ mg/L, $T = 25$ °C, $t = 1$ h and $m = 0.5$ g. It can be seen that when the pH increases from 1 to 2, the efficiency is very low. At a lower pH, both the concentration and the mobility of H^+ were high, which favored the protonation of the amino groups (Zaitsev & Kobylinskaya 2005). According to the Eh-pH diagram of nickel, nickel in acidic solutions mainly exists in the form of Ni(II) (Brookins 1988). Therefore, there was strong competition between the Ni and H ions toward the active sites on the adsorbent in strong acidic solutions. A sharp increase occurred over the pH range of 2–4. In this range, the amino groups were less protonated, and more active sites were available for Ni(II). With further increase in the pH, the adsorption reaches equilibrium, suggesting the adsorption sites on the adsorbent were fully occupied. It was observed that nickel ions precipitated from the solution when the pH was higher than 6. Therefore, the optimum pH selected for the following tests is 6. The corresponding maximum efficiency and ion retention are 85.29% and 4.26 mg/g, respectively.

Effect of temperature

Figure 3 indicates that under the conditions of $pH = 6$, $C_0 = 50$ mg/L, $t = 1$ h, $m = 0.5$ g, the removal efficiency increases from 74.48 to 93.74% when the temperature increases from room temperature (25 °C) to 40 °C. Further increasing the temperature from 40 to 60 °C, the efficiency only slightly

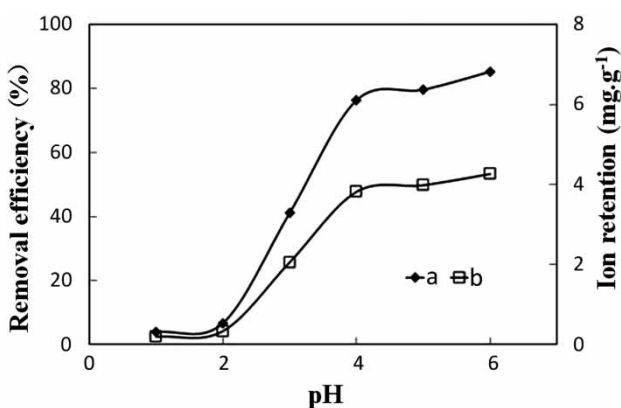


Figure 2 | The influence of pH on the efficiency and the adsorption capacity of the adsorbent ((a) removal efficiency; (b) ion retention).

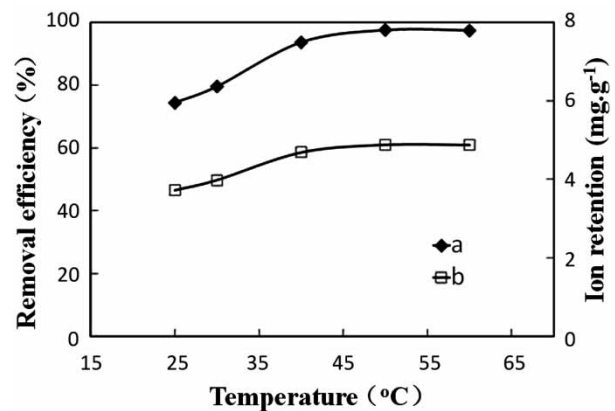


Figure 3 | Temperature dependence of the efficiency and adsorption capacity of the adsorbent ((a) removal efficiency; (b) ion retention).

increased. The efficiency and the ion retention at 60 °C are 97.53% and 4.88 mg/g, respectively. The results suggest that the adsorption of Ni(II) onto the amino-functionalized sand was an endothermic process (El Batouti & Ahmed 2014). The rise in the temperature increased the energy and mobility of the metal ions, and consequently there was more chance for the ions to be combined with the active sites on the adsorbents. However, since the increase of the efficiency with temperature was not so profound, to facilitate the experimental tests and save energy, the following tests were carried out at room temperature.

Effect of contact time

Figure 4 illustrates the variation of the removal efficiency with the contact time under the conditions of $C_0 = 50$ mg/L, $T = 25$ °C, $pH = 6$, $m = 0.5$ g. It can be seen that the adsorption increased rapidly during the first ten minutes.

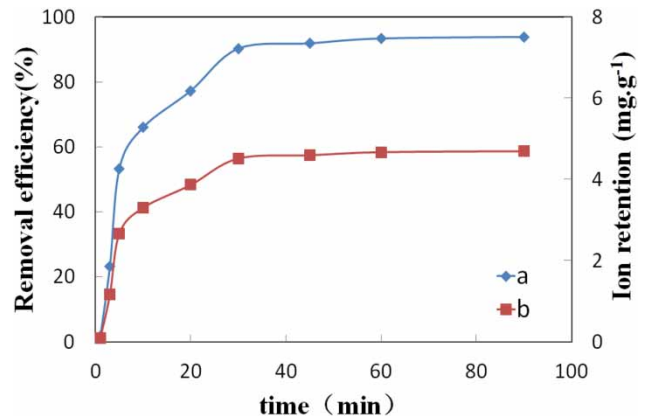


Figure 4 | The efficiency and adsorption capacity of the adsorbent at different contact times ((a) removal efficiency; (b) ion retention).

Up to 10 min, more than 50% of the Ni(II) in the solution has been adsorbed by the sand adsorbent. Afterwards, a gradual increase in the efficiency was observed between 10–30 min, followed by the adsorption equilibrium with an efficiency and ion retention of 90.29% and 4.51 mg/g, respectively. The observed three-stage variations in the

efficiency and the ion retention with contact time might be a reflection of the monolayer to multilayer adsorption mechanism (see later discussion about the adsorption models).

Effects of initial concentration and adsorbent dosage

As expected and shown in Figure 5, with a fixed dosage of 0.5 g sand adsorbent, the removal efficiency toward Ni(II) decreased with the initial concentration under the conditions of pH = 6, T = 25 °C, t = 1 h. This is due to the limited active sites for the adsorption. However, when the initial concentration increased from 3 to 150 mg/L, the ion retention increased from 0.3 to 5.78 mg/g.

Opposite to the variations with the initial concentration, the removal efficiency increased with the dosage of the sand adsorbent, while the ion retention decreased when the initial concentration was fixed at 50 mg/L. As shown in Figure 6, the removal efficiency increased from 17 to 100% using a dosage of the adsorbent from 0.1 to 3 g under the conditions of t = 1 h, T = 25 °C, pH = 6. It is understandable that more adsorbent provided more active sites for the adsorption.

Kinetic and adsorption models of the adsorption of Ni(II) onto the sand adsorbent

To explore the kinetics of the adsorption of Ni(II) onto the adsorbent, the time dependent removal efficiency data

Table 1 | Kinetic parameters for the adsorption of Ni(II) onto the developed sand adsorbent

| Pseudo-first-order model | | | Pseudo-second-order model | | |
|--------------------------|--------------------|--------|---------------------------|--------------------|-------|
| k_1/min^{-1} | $q_e(\text{mg/g})$ | R^2 | k_2/min^{-1} | $q_e(\text{mg/g})$ | R^2 |
| 0.0732 | 3.22 | 0.9758 | 0.046 | 4.97 | 0.993 |

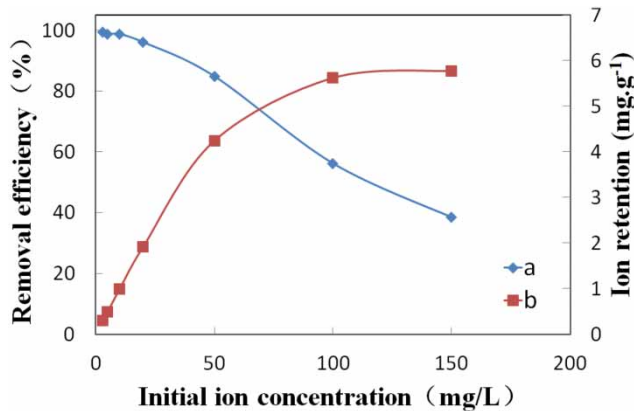


Figure 5 | Variation of the efficiency and adsorption capacity of the adsorbent with the initial ion concentration (a) removal efficiency; (b) ion retention).

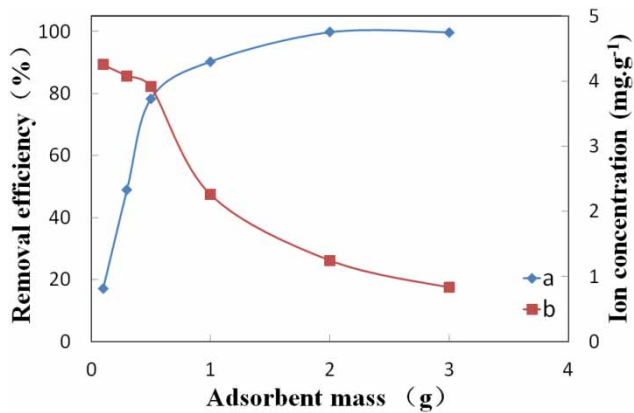


Figure 6 | The change of removal efficiency and adsorption capacity with the amount of silica sand (a) removal efficiency; (b) ion retention).

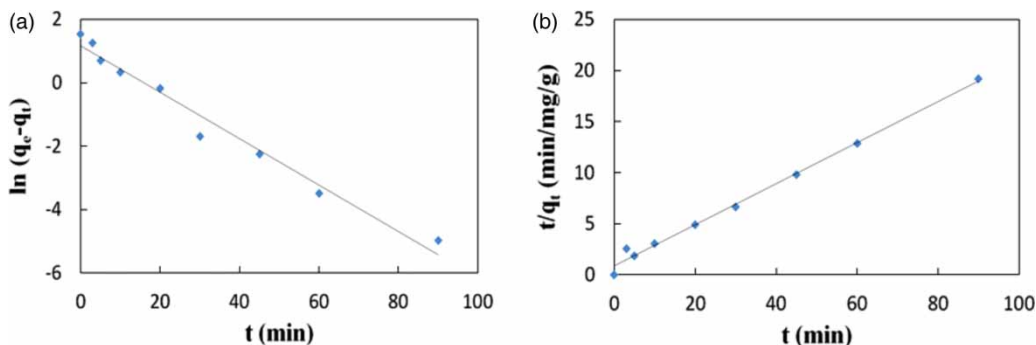


Figure 7 | Pseudo-first-order (a) and pseudo-second-order (b) modeling of the kinetics of the adsorption of Ni(II) onto the sand adsorbent ($C_0 = 50 \text{ mg/L}$).

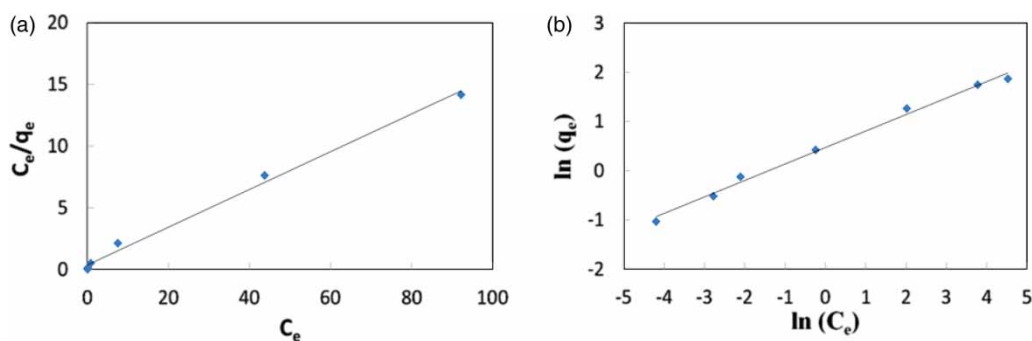


Figure 8 | Langmuir (a) and Freundlich (b) isotherms of the adsorption of Ni(II) onto the sand adsorbent.

Table 2 | Langmuir and Freundlich isotherm constants for the adsorption of Ni(II) onto the sand adsorbent

| Langmuir | | | Freundlich | | |
|------------------|--------------|--------|--------------|------|--------|
| Q_{max} (mg/g) | K_L (L/mg) | R^2 | K_F (mg/g) | n | R^2 |
| 6.527 | 0.41 | 0.9841 | 1.604 | 2.98 | 0.9931 |

were fitted with the pseudo-first-order and pseudo-second-order kinetic models. As is shown in Figure 7, the experimental data fit well with the pseudo-second-order model. The correspondent kinetic parameters are calculated and listed in Table 1. It can be seen that the correlation coefficient (R^2) based on the pseudo-second-order model is 0.993, much larger than that on the pseudo-first-order model. The results suggest that the adsorption of Ni(II) onto the sand adsorbent mainly took place through a chemical process involving valence forces through sharing or exchange of electrons (Ho & McKay 2003). However, the overall sorption rate was limited due to the slow rate of sorbate diffusion in the pores of the sorbent (Plazinski *et al.* 2013).

The data on the removal efficiencies against the equilibrium concentrations were used for the Langmuir and

Freundlich isotherms studies of the adsorption of Ni(II) on the sand adsorbent. The fitting results and the correspondent constants are shown in Figure 8 and Table 2, respectively. It is shown that the sorption data fit well to the Freundlich adsorption model, giving a linear plot with a regression value ($R^2 = 0.9931$) higher than that based on the Langmuir adsorption model ($R^2 = 0.9841$). The results also suggest that the adsorption of Ni(II) onto the sand adsorbent was a multi-layer adsorption (Dada *et al.* 2012). The $n = 2.98$ reflected a high heterogeneity of the adsorbent (Sočo & Kalembkiewicz 2013).

The reuse of the spent adsorbent

In colored glass production, the concentrations of colorants in glass batches are vital to generate a valid coloration. To guarantee that enough nickel could be brought by the spent adsorbent into the batch, the spent sand adsorbent was collected after the adsorption under the specified conditions. It was estimated that 84.89% of Ni(II) were removed from the solution. Based on the initial ion concentration, the volume of the solution and the adsorbent dosage, the adsorbed Ni(II) per unit mass of the adsorbent

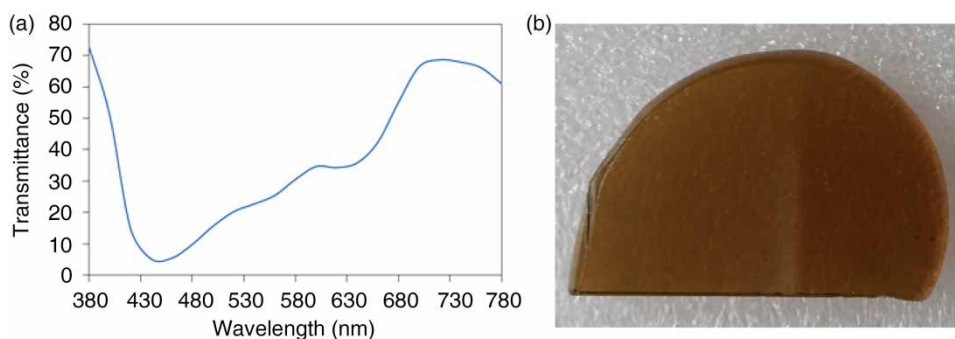


Figure 9 | The transmission spectrum (a) and the color glass (b) of the sample prepared with the spent sand adsorbent containing the adsorbed nickel.

was 4.24 mg/g. The spectrum and the sample of the glass prepared with the spent adsorbent containing the adsorbed Ni(II) is shown in Figure 9(a) and 9(b), respectively. It can be seen that the spectrum of the glass displays selective absorbance over the visible light region (Figure 9(a)). The distinct absorbance bands are located at 460–640 nm, which result in an apparently amber color (Scholze 1990) (Figure 9(b)).

CONCLUSIONS

A modified sand adsorbent with a porous silica coating and surface area of 150 m²/g was developed for the adsorption of nickel ions from aqueous solutions. The adsorption is pH dependent, with a sharp increase in the pH range of 2 to 4. The adsorption reaches equilibrium within 30 min. The maximum removal efficiency and ion retention in per unit mass of the adsorbent could be 100% and 5.78 mg/g under the specified experimental conditions. The kinetics and isotherm of the adsorption follow the pseudo-second-order and the Freundlich multilayer models, respectively. The spent adsorbent was successfully applied in preparing a brown colored glass. The present study provides a new adsorbent facilitating the reuse of the recovered nickel from wastewater.

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