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Review

Adsorption separation of Ni(II) ions by dialdehyde o-phenylenediamine starch from aqueous solution

Ping Zhao, Jian Jiang, Feng-wei Zhang, Wen-feng Zhao, Jun-tao Liu, Rong Li*

College of Chemistry and Chemical Engineering, Lanzhou University, No. 222, South Tianshui Roud, Lanzhou 730000, People's Republic of China

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ABSTRACT

Removal of nickel(II) ions from aqueous solution by using dialdehyde o-phenylenediamine starch (DASPDA) was investigated. The DASPDA was prepared from a reaction between dialdehyde starch (DAS) and o-phenylenediamine, and characterized by element analysis, FT-IR spectra and SEM. The FT-IR, results showed that DASPDA has different functional groups compared with DAS and these functional groups are able to react with metal ion in aqueous solution. Batch adsorption experiments were conducted to study the main parameters such as adsorption time, pH, initial Ni(II) ion concentrations and temperature. The adsorption results revealed that the optimal pH was 5.0, the equilibrium time was about 120 min, and the adsorption capacity increased with the increase of substitution DS (0.33, 0.49 and 0.90) of the DASPDA. Moreover, the Freundlich adsorption isotherm gave a satisfactory fit of the equilibrium, and the adsorption process is endothermic. The chelating of Ni(II) ions to DASPDA by adsorption is enhanced as the temperature increases.

Contents

1. Introduction

Heavy metal ions from sewage and industrial wastewater are of environmental concern due to their acute toxicity, non-biodegradable nature and build-up of high concentrations in water bodies all over the world (Mark et al., 2008). Various technolo-

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* Corresponding author. Tel.: +86 931 8912311; fax: +86 931 8912311.
E-mail address: liyirong@lzu.edu.cn (R. Li).

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gies have been developed to remove toxic metal ions from water over the years. The most important of these technologies include electro-deposition, chemical precipitation, membrane processing, solvent extraction, ion exchange and adsorption (Lee & Hong, 1995; Rivas, Pereira, Gallegos, & Geckeler, 2002). Among these methods, adsorption is considered as a powerful technique that was extensively used for removal of heavy metal ions from domestic and industrial effluents (Ali & Gupta, 2007; Gupta, Carrott, Ribeiro Carrott, & Suhas, 2009; Gupta, Rastogi, & Nayak, 2010a, 2010b). A number of workers have used different adsorbent systems, developed from various industrial waste materials, for the removal of toxic heavy metals and organic waste pollutants (Gupta, Ali, & Saini, 2004; Gupta, Jain, Ali, Chandra, & Agarwal, 2002; Gupta, Jain, Ali, Sharma, & Saini, 2003; Gupta & Rastogi, 1999; Gupta, Saini, & Jain, 2005; Gupta, Shrivastava, & Jain, 2001; Gupta, Shrivastava, Mohan, & Sharma, 1998; Gupta, Singh, & Rahman, 2004). These adsorbents have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems (Ajmal, Rao, Ahmad, & Ahmad, 2000; Aksu, 1998; Patterson, 1977; Wong, Wong & Tam, 2000). There still exists a need to develop a low cost and efficient adsorbent material for the removal of pollutants.

In recent years, biopolymers represent an interesting and attractive alternative as cheaper and more effective sorbents (Gupta et al., 2008, 2009; Gupta, Ali, Suhas, & Saini, 2006; Gupta & Rastogi, 2008a, 2008b, 2008c, 2008d). Among these biopolymers, polysaccharides deserve particular attention (Crini, 2005). As a natural polysaccharide, adsorbents based on starch have become a focus of study owing to starch's renewable and biodegradable properties. A variety of different approaches have been used to modify starch as a metal absorbent (Crini, 2005). An effective method is the chemical modification (including esterification, etherization or oxidation) of carboxylate (Khalil & Abdel-Halim, 2001; Xu, Feng, Peng, Wang, & Yushan, 2005; Xu, Feng, Yue, & Wang, 2004; Xu, Zhang, Lu, Yang, & Cui, 2003), xanthate (Bose, Bose, & Kumar, 2002), phosphate (Guo, Zhang, Ju, & Yang, 2006), acrylamide (Chauhan, Singh, & Sharma, et al., 2006) and acrylonitrile (Abdel-Aal, Gad, & Dessouki, 2006). Dialdehyde starch (DAS) was obtained from the periodate oxidative cleavage of the C(2)–C(3) bond of the anhydroglucose units of starch polysaccharide chains. Since aldehyde groups form hemiacetals and acetals, their good cross-linking ability has rendered DAS great industrial application potentials especially as a component of biodegradable plastics for packing purposes and wet-strength additive of tissue-paper (Tomasik & Schilling, 2004; Veelaert, Wit, Gotlieb, & Verhe, 1997). Recently, it was shown that dialdehyde starch dithiosemicarbazone (Para & Ropek, 2000), disemicarbazone (Ropek & Para, 2002) and dihydrazone (Para, Karolczyk-Kostuch, & Fiedorowicz, 2004) could form stable complexes with heavy metals. For example, complex formation from dialdehyde aminothiazole starch and Cu(II) ions and its adsorption properties in aqueous solution have been reported by Yin, Ju, Zhang, Wang, and Yang (2008).

Biocompatible polysaccharide polymers, such as, chitosan, have been found to be capable of chemically or physically entrapping various metal ions due to high concentration of amino and hydroxyl groups in the polyaminoglucosan chain (Schiewer & Wong, 2000). The chelate formed from polymeric ligands was characterized by reactive functional groups containing O, N, donor atoms and its capability of coordinating to different metal ions was extensively studied. Schiff bases with N and O as donor atoms are well known to form strong complexes with transition metal ions. Many Schiff bases were reported to form strong complexes with a specific ion due to geometric factors (Reglinski, Morris, & Stevenson, 2002). Recently, many polymer matrixes containing Schiff base (Samal, Acharya, Dey, et al., 2002) ligands were found to adsorb Ni(II) ions.

In the present work, Schiff base type starch dialdehyde o-phenylenediamine (DASPDA) was synthesized by the reaction of o-phenylenediamine and dialdehyde starch (DAS) from the oxidation of potato starch by periodate. The aim of the work was to prepare starch DASPDA with different DS and to determine the ability of these adsorbents in removing nickel(II) ion from aqueous medium. Batch adsorption experiments were carried out as a function of adsorption time, pH, initial Ni(II) ions concentrations and temperature. The adsorption isotherm and thermodynamics parameters of the adsorption were also investigated.

2. Experimental

2.1. Materials and apparatus

Potato starch (food-grade) was dried at 105 °C before using. $Ni(NO_3)_2$ and NaOH were obtained from Xi'an Chemical Factory (Xi'an AR China). $NaIO_4$ and o-phenylenediamine (AR) were purchased from Tianjing Chemical Factory (Tianjing AR China). All the other commercial chemicals were of analytic reagent grade and used without further purification. Infrared spectra were obtained by the KBr disc technique and were recorded on NEXUS670. The element analyses for C, H and N were performed on a VarioEL. The morphology of samples was observed with a JSM-5600LV scanning electron microscopy (SEM) operated at 20 kV. Atomic adsorption spectrometry was carried out using an AAnalyst 240 instrument (Varian American).

2.2. Preparation of dialdehyde starch and determination of aldehyde content

Dialdehyde starch (DAS) was prepared according to Yin et al. (2008). Three kinds of DAS, designated as DAS1, DAS2 and DAS3, respectively, were prepared and the degree of oxidation was controlled by the addition of $NaIO_4$ (0.03, 0.05 or 0.09 mol). The aldehyde group content was determined using the rapid quantitative alkali consumption method (Hofreiter, Alexander, & Wolff, 1955) and the results were 32%, 48% and 87% for DAS1, DAS2 and DAS3, respectively.

The percentage of dialdehyde units was given by the equation:

$$Da\% = \frac{(V_1C_1 - 2V_2C_2) \times 100\%}{W/161}$$

where V_1, V_2 and W represent the total volumes (L) of H_2SO_4, NaOH and the dry weight (g) of the oxidized starch, respectively. C_1, C_2 (mol/L) represent the concentrations of H_2SO_4 and NaOH. 161 is the average molecular weight of the repeat unit in dialdehyde starch.

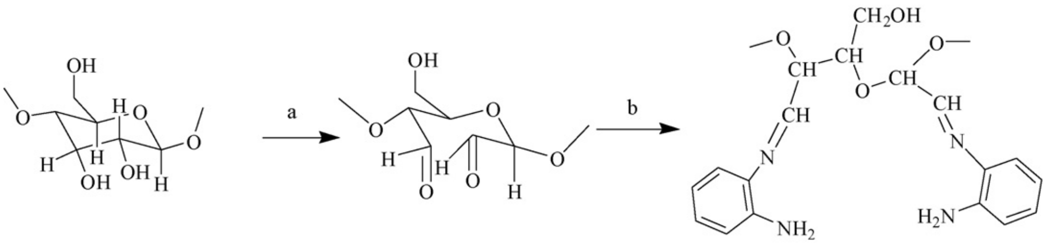
2.3. Preparation of starch dialdehyde o-phenylenediamine

6.5 g of DAS was slurried in 50 mL distilled water in a two-necked flask, which was equipped with an electromagnetic stirrer and thermostat oil bath. Then, 50 mL of o-phenylenediamine solution with a molar ratio of 2:1 to dialdehyde was slowly added into the flask under nitrogen protection. The pH value of the mixture was adjusted to 5.0 with acetic acid. The mixture was stirred for 4 h at 55 °C on an oil bath. The slurry was filtered and extensively rinsed with distilled water and with ethanol for one time, the product was then dried at 50 °C in vaccum.

The reaction process of dialdehyde o-phenylenediamine starch is shown in Scheme 1.

2.4. Analysis of adsorbents

The substitution degree of o-phenylenediamine for DASPDA was theoretically calculated from the nitrogen content using the following equation: $Ds = 161 \times N\%/(2800 - 90.14 \times N\%)$. The results of the element analyses and the yield of condensation products are



Scheme 1. Preparation process of the dialdehyde o-phenylenediamine starch. Reagents and conditions: (a) $NaIO_4$; (b) o-phenylenediamine.

listed in Table 1. It is evident that the nitrogen content in DASPDA increased markedly with the increase of dialdehyde percentage in DAS. The DS of o-phenylenediamine which represents the average molecular number of the repeat unit in DASPDAs is 0.33, 0.49 and 0.90 for DASPDA1, DASPDA2 and DASPDA3, respectively.

2.5. Adsorption experiments

The adsorption of nickel(II) ions on DASPDA was studied by batch technique. A known weight of DASPDA (0.15 g) was equilibrated with 50 mL of aqueous $Ni(NO_3)_2$ solution with 19.5 mmol/L in a 100 mL Erlenmeyer flask at 20 °C in a shaking bath. The initial pH was adjusted with 0.1 M HNO_3 or 0.1 M NaOH before adding the adsorbent. After shaking for 120 min to ensure full equilibration, the mixture was filtered and final concentration of nickel(II) was determined by atomic adsorption spectrophotometer.

The adsorption capacity was calculated from the following expressions:

$$Q = \frac{(C_i - C_t)V}{m}$$

where Q is the adsorption capacity of the adsorbent (mmol/g), C_i and C_t (mol/L) are the initial and terminal concentrations of the Ni(II) ions in the adsorption solution, and V (mL) and m (g) are the volumes of the adsorption solution and the dose of the adsorbent, respectively.

3. Results and discussion

3.1. Characterization of the prepared DASPDA

3.1.1. The FT-IR spectra of DAS and DASPDA

FT-IR spectra were recorded on KBr pellet using NEXUS670. As shown in Fig. 1, the IR spectra of DAS showed bands at 1732, 2859, and 2924 cm^{-1} corresponding to the stretching vibrations of the C=O and C–H bonds, respectively. In comparison to DAS, the IR spectra of DASPDA appeared new bands that represent phenylenediamine groups bound to the DAS. So the diagnostic peaks appeared on the DAS-Schiff base at 1601 and 3351 cm^{-1} were due to the stretching vibrations of the C=N bonds and C–N bonds.

3.1.2. Surface morphology of DASPDA

The SEM images of potato starch, DAS3, DASPDA3 and DASPDA3 adsorbed Ni(II) ions display a rough structure on surface (Fig. 2). Photographs of representative areas of the samples were taken at 500 (Fig. 2a, c, e and g) and 1000 (Fig. 2b, d, f and h) magnifications. The original potato starch particles (Fig. 2a and b) showed smooth and dispersed, but after oxidization by periodate the particles (Fig. 2c and d) became diverse. Obviously, the cleavage of glucoside rings leads to an altered uneven surface, creating pores on the particles. Also notable was that the particles were conglomerated closely, and the granules became much bigger than the original starch. DASPDA (Fig. 2e and f) after reacting with phenylenediamine showed particle fragments and irregular structure due to reduction or loss of cross-linking. Fig. 2g and h shows micrographs of the DASPDA after a Ni(II) ions adsorption, which indicated that the fragments became much smaller than the DASPDA, and had no clear diversification in comparison to DASPDA.

Table 1
Degree of substitution of DASPDA.

Product	Reactant	Color	Elemental analysis			Ds
			N (%)	C (%)	H (%)	
DASPDA1	DAS1	Yellow	4.816	47.57	5.446	0.33
DASPDA2	DAS2	Yellow	6.670	48.30	6.092	0.49
DASPDA3	DAS3	Yellow	10.440	54.47	6.228	0.90

3.2. Adsorption of Ni^{2+} ions

3.2.1. Effect of initial pH

One of the most important factors affecting DASPDA adsorption capacity of metal ions is the acidity of solutions. The acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the adsorption surface (Lodeiro, Barriada, Herrero, & Sastre de Vicente, 2006). Different metal ions may have different pH optima, possibly due to the different solution chemistry of the species (Gupta et al., 2010a, 2010b). Since at the initial Ni^{2+} concentration, $Ni(OH)_2$ can precipitate at pH 6.78 ($pK_{sp} = 15.26$), the effect of initial pH on the equilibrium uptake of nickel(II) ions was investigated between pH 2.0 and 7.0 (Fig. 3).

Negligible adsorption could be found at a lower pH range of 2.0–3.0. The adsorption then increased gradually with pH increasing from 4.0 to 6.0. The low level of nickel(II) uptake at lower pH values could be due to that the adsorbents which were highly

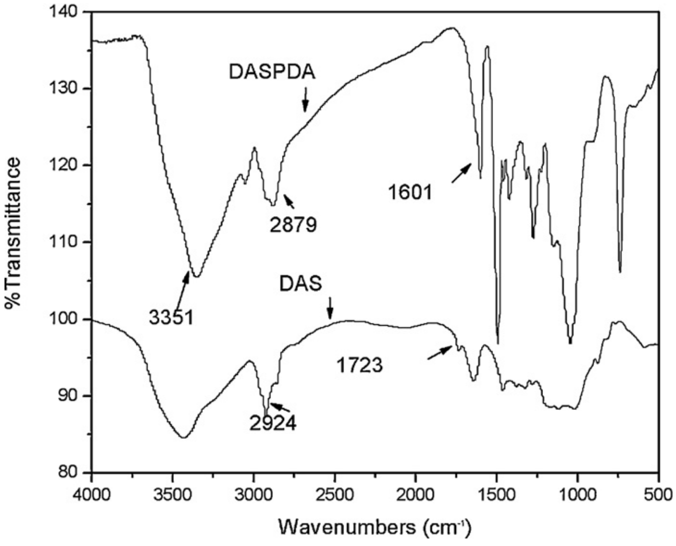


Fig. 1. FT-IR spectra of DAS and DASPDA.

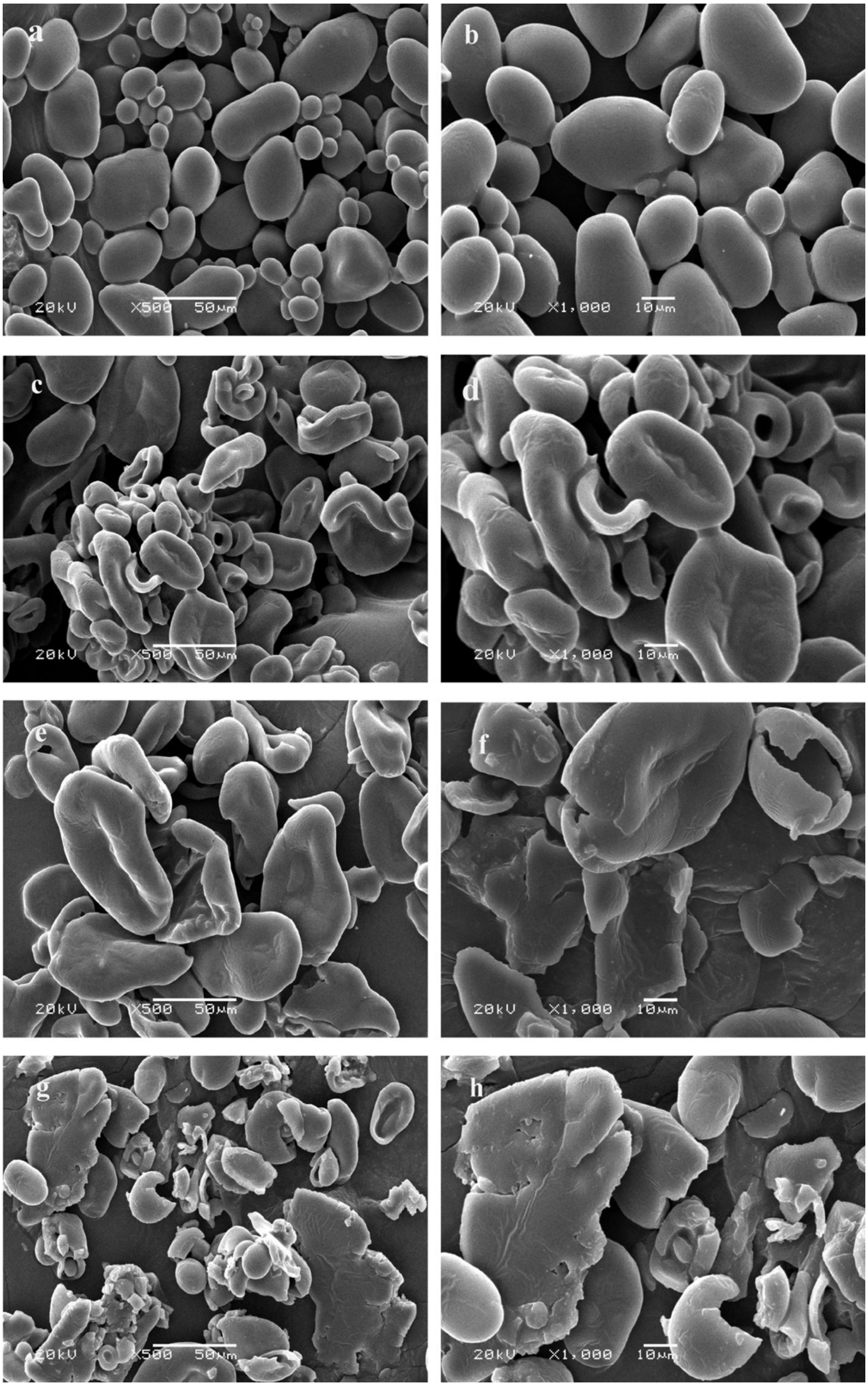


Fig. 2. SEM images of different starch granules. (a and b) Potato starch; (c and d) DAS3; (e and f) DASPDA3; (g and h) DASPDA3 adsorbed Ni(II) ions. The scale bar is 50 µm for (a), (c), (e) and (g) and 10 µm for (b), (d), (f) and (h).

protonated in an acid medium can not effectively interact with the metal ions because the increased proton concentration in the medium inhibited the metal–chelate complex of the adsorbent. The increase in nickel(II) adsorption at higher pH values (4.0–6.0) may be explained by the ionization of functional groups on the chelate surface which involves competitive reactions of protonation and complex binding (Juang & Chen, 1996). The same trends were indicated at different DS (0.33, 0.49 and 0.90) of the amino groups. At the same pH value, the adsorption capacity of the adsorbent augments with the increase of DS of the phenylenediamine groups, i.e. $Q_{DASPDA1} < Q_{DASPDA2} < Q_{DASPDA3}$. The phenylenediamine groups are the main factor in the adsorption procedure, so the adsorp-

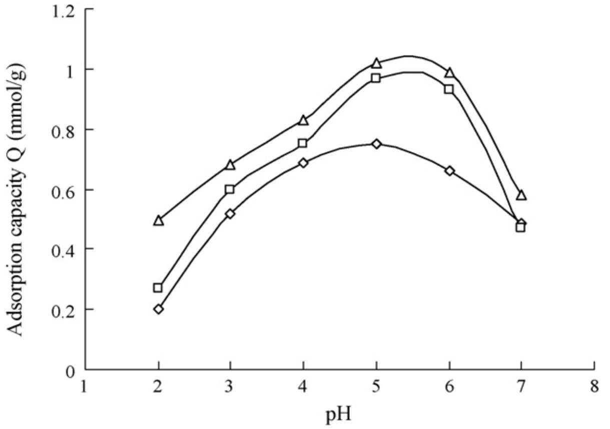


Fig. 3. Effect of initial pH value of the solutions on adsorption capacity. (◊) DASPDA1; (□) DASPDA2; (△) DASPDA3. $[Ni(NO_3)_2]$ = 19.5 mmol/L; t = 2 h; T = 25 °C; the dose of each DASPDA is 0.15 g.

tion is more effective when the DS of phenylenediamine groups is higher. As the pH is lowered, the overall surface charge on the chelate will become positive, which will prevent the approach of positively charged metal cations. However, when the pH value continued to increase up to 7.0, the adsorption capacity decreased, which is due to the formation of soluble hydroxilated complexes of the metal ions which compete react with the active sites, and as a consequence, the retention would decrease again. Previous studies also reported that the maximal biosorption efficiency for Ni(II) metal ion on biomass was observed at pH 5 (Chen, Ma, & Han, 2008; Saygideger, Gulnaz, Istifli, & Yuc, 2005; Sheng et al., 2004; Vijayaraghavan, Jegan, Palanivelu, & Velan, 2005; Wong et al., 2000; Yu & Kaeswarn, 2000).

3.2.2. Effect of adsorption time

To establish an appropriate treatment time between DASPDA and Ni(II) ions solution, adsorption capacities of Ni(II) were measured as a function of time. As shown in Fig. 4, the adsorption capacities of Ni(II) for adsorption times ranging from 30 to 120 min at 25 °C increases with the treatment time within the first 2 h. However, the adsorption capacity slightly decreased as the adsorption time reached 80 min. The reduced metal-adsorption was possibly caused by the increased amount of dissolved starch. This initial 30 min quick phase was followed by slow attainment of equilibrium as a large number of vacant binding sites would initially be available for adsorption; but thereafter, the occupation of the remaining vacant sites would be difficult due to the repulsive forces between the metal ions in the solid and bulk phases. After 120 min, the metal ions should access to equilibrium.

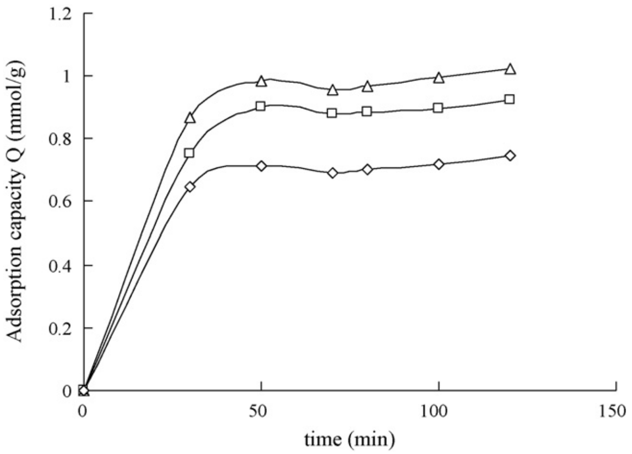


Fig. 4. Effect of adsorption time: (◊) DASPDA1; (□) DASPDA2; (△) DASPDA3. $[Ni(NO_3)_2]$ = 19.5 mmol/L; pH 5.0; T = 25 °C; the dose of each DASPDA is 0.15 g.

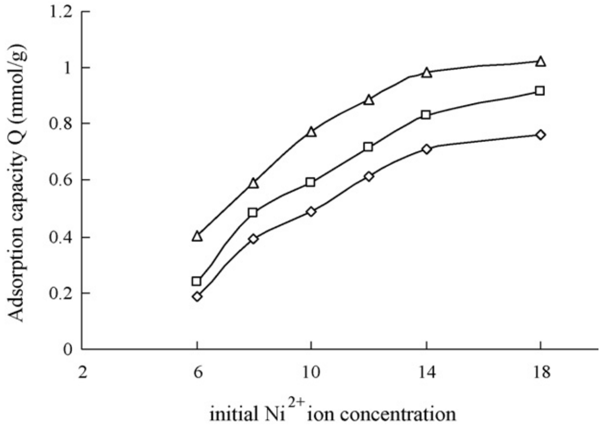


Fig. 5. Effect of initial concentration of Ni(II) on (◊) DASPDA 1; (□) DASPDA2; (△) DASPDA3. t = 2 h; pH 5.0; T = 25 °C; the dose of each DASPDA is 0.15 g.

3.2.3. Effect of the initial Ni(II) ions concentration

The relationship between the initial Ni(II) ion concentration and the adsorption capacities of DASPDA for Ni(II) was studied. As shown in Fig. 5, the adsorption capacities of DASPDA1, DASPDA2, and DASPDA3 for Ni(II) were positively correlated with the initial Ni(II) ion concentration because the adsorption process was highly concentration dependent. When the initial Ni(II) ion concentration was increased from 6.0 mmol/L up to 18.0 mmol/L, the adsorption capacity of DASPDA1, DASPDA2, and DASPDA3 increased from 0.188 to 0.753 mmol/g, 0.239 to 0.953 mmol/g, and 0.405 to 1.01 mmol/g, respectively. The increasing adsorption capacity of DASPDA is probably due to a high DS of the phenylenediamine groups. Moreover, they share a common trend, which implies that the type of adsorption isotherms for the three adsorbents may be the same.

3.3. Adsorption isotherm

Among various plots employed for analyzing the nature of adsorbate–adsorbent interaction, adsorption isotherm is the most significant. The results of adsorption studies of nickel at different concentrations ranging from 2 to 18 mmol/L on a fixed amount of adsorbent were expressed by isotherm theories.

The Freundlich isotherm is an empirical equation based on an exponential distribution of sorption sites and energies. In mathematical form, it is represented as:

$$Q_e = K_f {C_e}^{1/n}$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

In the above equations, C_e and Q_e are equilibrium Ni(II) ion concentration (mmol/L) and equilibrium adsorption capacity (mmol/g), respectively; K_f and n are Freundlich constants, which affect the adsorption process such as adsorption capacity and intensity of adsorption, respectively. The model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption. Fig. 6 depicts the plots obtained by the Freundlich isotherm for the adsorbents along with their R^2 values. The Freundlich constants for adsorbents were calculated and presented in Table 2.

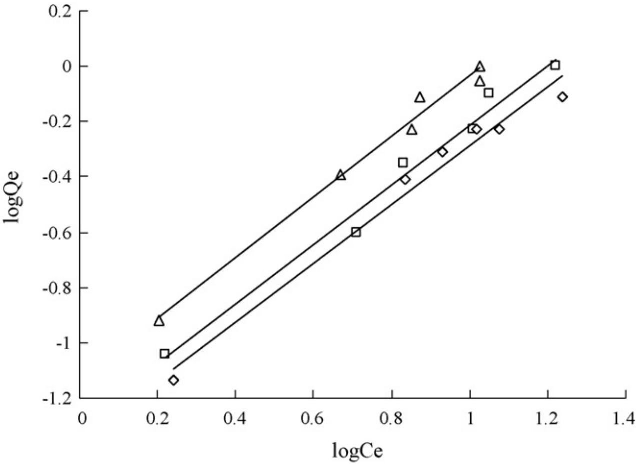


Fig. 6. Freundlich isotherm for the adsorption of Ni(II) ions on (◊) DASPDA1; (□) DASPDA2; (△) DASPDA3. $[Ni(NO_3)_2]$ = 19.5 mmol/L; pH 5.0; t = 2 h; the dose of DASPDA3 is 0.1 g.

Table 2
Freundlich parameters for three kinds of DASPDAs.

Sample	K_f	n	R^2
DASPDA1	0.0738	0.9412	0.9797
DASPDA2	0.0512	0.9295	0.9818
DASPDA3	0.0449	0.9134	0.9872

3.3.1. Thermodynamic studies

The adsorption behavior of adsorbed Ni(II) on the adsorbents at different temperatures ranging from 25 to 65 °C was also investigated (Fig. 6). The results show that as the temperature increased, the value of Q increased, which implied that the adsorption process was endothermic. To certify this conclusion, the curves of $\log(Q/C_e)$ versus $1/T$ for DASPDA3 is shown in Fig. 7. Because the relation between $\log(Q/C_e)$ and $1/T$ for DASPDA3 is linear (Fig. 8), the changes of apparent enthalpy (ΔH^θ) and entropy (ΔS^θ) were determined using the following equations:

$$\log \frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R}$$

The change of adsorption free energy (ΔG^θ) was calculated by the thermodynamic equation:

$$\Delta G^\theta = \Delta H^\theta - T\,\Delta S^\theta$$

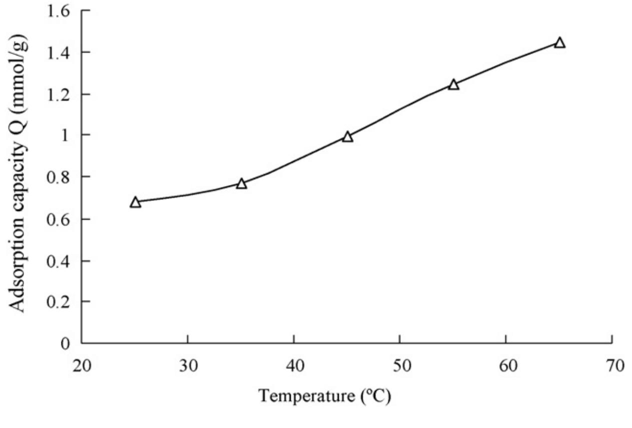


Fig. 7. Effect of adsorption temperature for DASPDA3. $[Ni(NO_3)_2]$ = 19.5 mmol/L; pH 5.0; t = 2 h; the dose of DASPDA3 is 0.1 g.

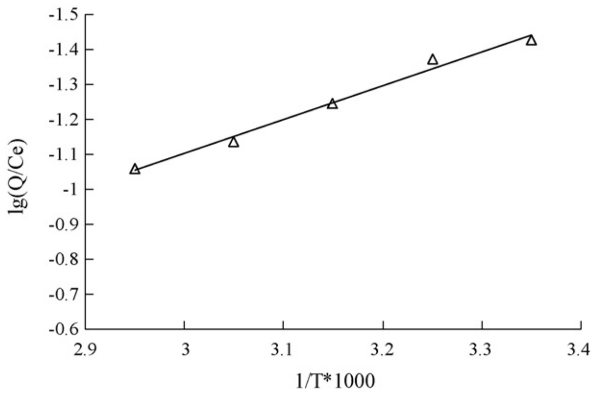


Fig. 8. $\log(Q/C_e) \sim 1/T \times 1000$ for DASPDA3. $[Ni(NO_3)_2]$ = 19.5 mmol/L; pH 5.0; t = 2 h; the dose of DASPDA3 is 0.1 g.

Table 3
Thermodynamic parameters for DASPDA3.

Temperature (°C)	ΔG^θ (kJ/mol)	ΔH^θ (kJ/mol)	ΔS^θ (J/mol)
25	3.533	18.502	34.367
35	3.516		
45	3.397		
55	3.015		
65	2.980		

The calculated values of the thermodynamic parameters, such as, ΔH^θ, ΔS^θ and ΔG^θ are listed in Table 3. It can be observed that ΔG^θ decreases with the increase of temperature, and the adsorption is more favorable at high temperatures. The positive value of ΔH^θ indicated that the adsorption was endothermic and higher temperature makes the adsorption easier. In addition, the positive value of ΔS^θ indicates that there is an increase in the randomness at the solid/solution interface during the adsorption process.

4. Conclusions

Starch dialdehyde o-phenylenediamine was synthesized by the reaction of o-phenylenediamine and dialdehyde starch (DAS) obtained from potato starch oxidation by periodate. The data obtained through this work supports that the DASPDA is an effective low-cost adsorbent for the removal of nickel ions from aqueous solution. The adsorption behavior is dependent on the pH of the solution, the initial concentration of Ni^{2+} ion, as well as the adsorption temperature. Maximum removal of nickel on DASPDA is at pH 5.0. Moreover, adsorption reaches equilibrium in about 120 min. The adsorption follows the Freundlich isotherm. The adsorption capacity increases with the increasing DS of the DASPDA. The maximal adsorption capacities of DASPDA1, DASPDA2 and DASPDA3 used in this study are 0.761 mmol/L, 0.967 mmol/L, and 1.03 mmol/L for nickel at 25 °C, respectively. The adsorption process of DASPDA3 is endothermic, and the apparent enthalpy (ΔH^θ) is 18.50 kJ/mol. DASPDA gave a potential application as a low-cost and effective absorbent.

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