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Adsorption of nitrophenol compounds from aqueous solution by cross-linked starch-based polymers

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ABSTRACT

Two kinds of cross-linked starch polymers were synthesized and used as adsorbent materials for the adsorption of o-nitrophenol (o-NP), p-nitrophenol (p-NP), 2,4-dinitrophenol (2,4-DNP) and 2-s-butyl-4,6-dinitrophenol (DNBP) from aqueous solutions. Results from adsorption experiments showed that the polymer 1 prepared by 4,4´-methylene-bis-phenyldiisocyanate (MDI) as cross-linking agent exhibited higher adsorption behaviors than that of the polymer 2 prepared by hexamethylene diisocyanate (HMDI). Equilibrium and thermodynamic of four nitrophenols on polymer 1 were further studied. Analyzed experimental data showed that the Freundlich model fitted the isotherm data better than the Langmuir model of the four nitrophenols onto polymer 1. The thermodynamics for the adsorption of the nitrophenols on polymer 1 were estimated in the range of 303–333 K. It has been found that the values of Gibbs free energy (ΔG) became more negative with decreasing temperature, which indicated that the adsorption process was more favorable at low temperature.

Keywords: Cross-linked starch polymers; Nitrophenols; Adsorption

1. Introduction

Nitrophenols are widely recognized to be a group of persistent organic pollutants (POPs) of low biodegradability with serious risks to human health and the environment. Among the nitrophenols, o-nitrophenol (o-NP), p-nitrophenol (p-NP), 2,4-dinitrophenol (2,4-DNP), and 2-s-butyl-4,6-dinitrophenol (DNBP) are classified as toxic organics by the US Environmental Protection Agency [1]. They are manufactured in large quantities, most being used as effective inhibitors of the styrene polymerization in chemical industry and as herbicides in agriculture [2,3]. With a large amount of industrial wastewater being produced, there is an increasing demand for the removal of nitrophenols.

Different methods have been developed for the removal of nitrophenols from sewage and industrial wastewater, such as biodegradation process [4], denitrification process [5], membrane process [6], photocatalytic degradation [7,8], fenton process [9], chemical and electrochemical techniques [10,11], and adsorption [12–16]. Despite the availability of the above-mentioned processes, the adsorption method is generally preferred due to its high efficiency, easy handling, and availability of different adsorbents.

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Starch is abundant, biodegradable, and renewable and has the capacity to associate by physical and chemical interactions with a wide variety of molecules. Recently, adsorbents based on starch have attracted more and more attention with the aim to develop low-cost adsorbents. A variety of starch and starch derivatives cross-linked with phosphate [17], aminothiazole [18], amino [19], carboxymethyl [20], acrylonitrile [21], acrylamide [22], and other agents [23] have been prepared and utilized to remove the pollutants from water. Many studies have been reported in the literature about the use of starch derivatives as potential adsorbents for the removal of metal contaminants from aqueous solutions, such as Cr(VI), Cu(II), Zn(II), Ni(II), Hg(II), and Pb(II) [24–29]. However, research studies on adsorption of organic compounds by starch-based adsorbent are limited [30,31].

The main objective of this study was to evaluate the adsorption potential of cross-linked starch-based polymers for nitrophenol compounds from aqueous solution. Two kinds of cross-linked starch polymers were synthesized using 4,4´-methylene-bis-phenyldiisocyanate (MDI) and hexamethylene diisocyanate (HMDI) as cross-linking agent. The adsorption behaviors of o-nitrophenol (o-NP), p-nitrophenol (p-NP), 2,4-dinitrophenol (2,4-DNP), and 2-s-butyl-4,6-dinitrophenol (DNBP) on the cross-linked starch polymers were investigated in detail. Various isotherm models (Langmuir, Freundlich, Dubinin–Redushkevich) based on the correlation coefficient were evaluated to better understand the adsorption mechanism. The thermodynamics for the adsorption was also investigated.

2. Materials and methods

2.1. Materials

Starch (analytic reagent grade) purchased from aladdin Corp (Shanghai, China) was dried before it was used. 4,4´-methylene-bis-phenyldiisocyanate (98%), N,N-dimethylformamide (98%), hexamethylene diisocyanate (99.5%), and acetone (guaranteed reagent) were also purchased from aladdin Corp (Shanghai, China) and used without further purification. O-nitrophenol (o-NP), p-nitrophenol (p-NP), 2,4-dinitrophenol (2,4-DNP), and 2-s-butyl-4,6-dinitrophenol (DNBP) with analytical grade were from Tianjin Guangfu Chemical Corp., Tianjin, China.

2.2. Preparation of cross-linked starch polymers

The cross-linked starch-based polymers were prepared in one step using MDI or HMDI as cross-linking agent. The synthetic method developed by Yilmaz was adopted with some modifications [32]. A typical reticulation reaction was carried as follows. The weight of 2.0 g of starch was dissolved in 10 mL of dry N,N-dimethylformamide (DMF) at room temperature. The temperature was raised gradually to 70℃, and 1.46 g of 4,4-methylene-bis-phenyldiisocyanate (MDI) or 1.0 g hexamethylene diisocyanate (HMDI) were dropped to the mixture solution. The suspension was maintained under stirring for 120 min at the same temperature. The reaction was stopped by addition of enough acetone to cover the mixture. The precipitation was filtered and washed using acetone and purified water several times successively. Then the precipitation was purified by soxhlet extractor for 24 h using acetone as extractant. After drying overnight at 40℃ in a vacuum oven, the polymers were ground and sieved. The cross-linked starch polymers prepared by MDI and HMDI were named as polymer 1 and polymer 2, respectively.

2.3. Analyses

The Fourier transform infrared (FT-IR) spectra of the native starch and cross-linked starch polymers were recorded on a Tensor 27 spectrophotometer (Bruker, Germany). Potassium bromide (KBr) disks were used to prepare the samples, which is mixed with starch with the ratio of 1:20. The samples were scanned from 500 to 4,000 cm^{-1}.

Thermo gravimetric analysis (TGA) of native and cross-linked starch polymers was performed using thermal analysis (STA 449 F3, Netzsch, Germany). Samples of approximately 5 mg were heated in an aluminum cell between 30 and 800℃ temperature at a heating rate of 10℃ min^{-1} under nitrogen atmosphere.

X-ray diffraction (XRD) patterns were recorded on a PANalytical X′pert diffractometer with Cu-Ka radiation at 40 kV and 40 mA. The angle (2θ) was in the range of 10–90° and a scanning speed was 5° min^{-1}.

The morphological features of native starch and cross-linked starch polymers were observed with field emission scanning electron microscopy (FESEM, Hitachi S4800). The dried samples were coated with gold to make the sample conductive.

The cross-linked starch polymers were also characterized by N_2 adsorption using a Micromeritics ASAP 2010 surface area analyzer. Prior to the analysis, the sample was outgassed at 150℃ for 5 h to a residual pressure of 10^{-4} torr or less.

2.4. Adsorption experiments

Adsorption studies were performed by the batch technique to obtain equilibrium data. Batch sorption test were carried out with amount of cross-linked starch polymers and 30 mL nitrophenols solutions at known concentrations in tightly closed flasks. The pH value was adjusted using either 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The mixture suspensions were stirred on a horizontal shaker at a constant agitation speed of 150 rpm and the adsorption temperature was controlled by an oven oscillator (Taicang Instrument Manufacturing Co. Ltd., China). The supernatant solutions were centrifuged at 2,500 rpm for 5 min to remove any adsorbent particles before measurement. The residual concentrations of o-NP, p-NP, 2,4-DNP, and DNBP were measured spectrophotometrically (Rayleigh UV1201, Beijing Rayleigh Analytical Instrument Corp., China) at wavelengths of 279, 317, 357, and 375 nm, respectively [9,16]. Blank samples without

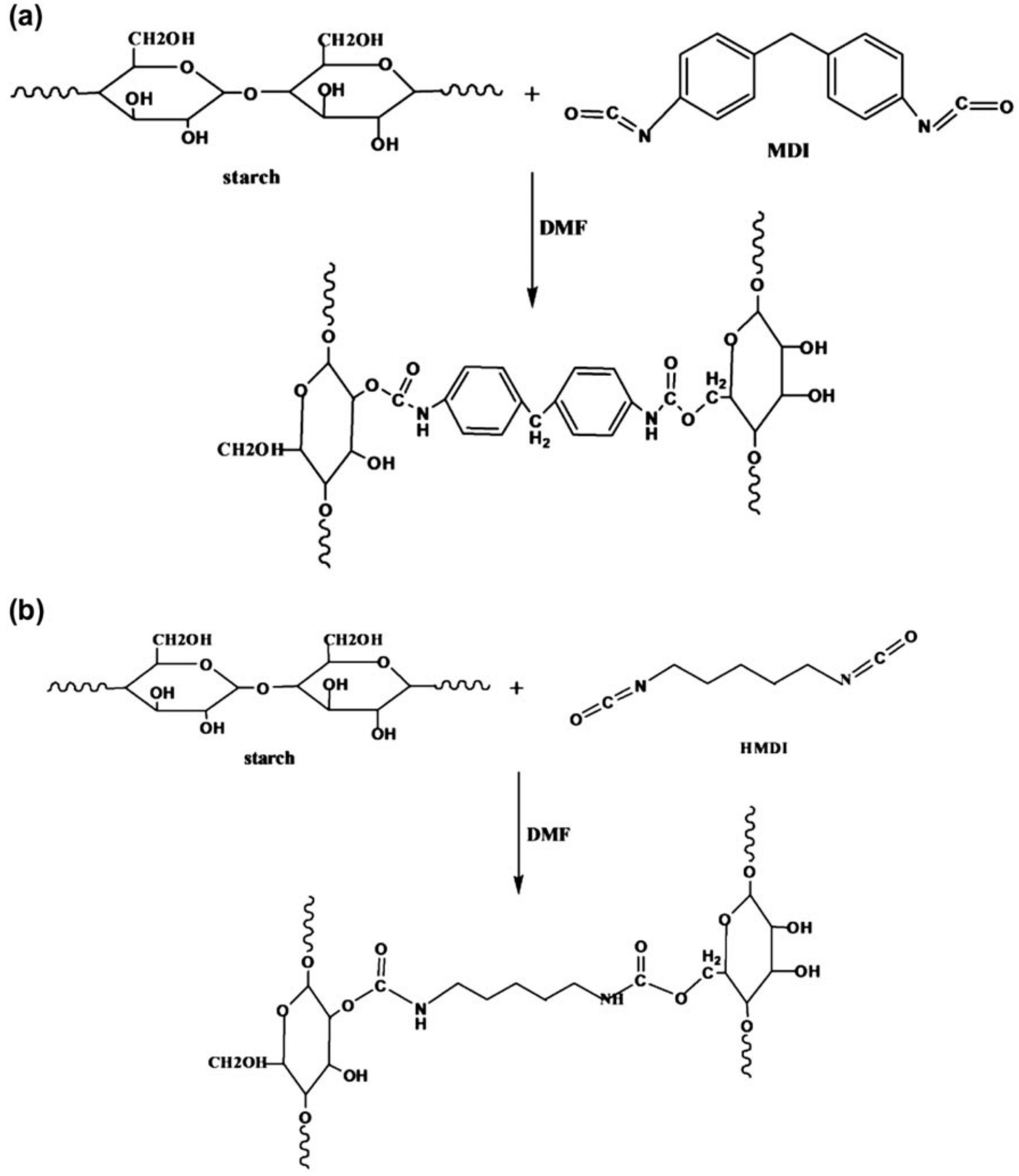

Fig. 1. The preparation procedure of the polymer 1 (a) and polymer 2 (b).

adsorbent were used for comparison under the same conditions. Adsorption isotherms were plotted and the sorption capacities of the absorbent towards o-NP, p-NP, 2,4-DNP, and DNBP were evaluated. The amount of solute adsorbed onto cross-linked starch polymers at equilibrium was calculated based on Eq. (1) and the calculated adsorption efficiency was given by Eq. (2)

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\text{Adsorption efficiency } (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

3. Results and discussion

3.1. Characterization of cross-linked starch based polymers

In this study, the cross-linked starch polymers were prepared based on the cross-linking reaction of native starch with MDI or HMDI as cross-linking agent, and the preparation procedures are shown in Fig. 1. Cross-linking occurred when the cross-linking agent was introduced as intermolecular bridges between polysaccharide macromolecules. Cross-linking drastically reduced segment mobility in the polymers and a number of chains were interconnected by the formation of new interchain linkages [33]. The formed dimensional networks can improve their adsorption properties. Characterization of the polymers was confirmed by combination of Fourier transform infrared spectra (FT-IR) analysis, TGA, XRD, and scanning electron micrographs (SEM).

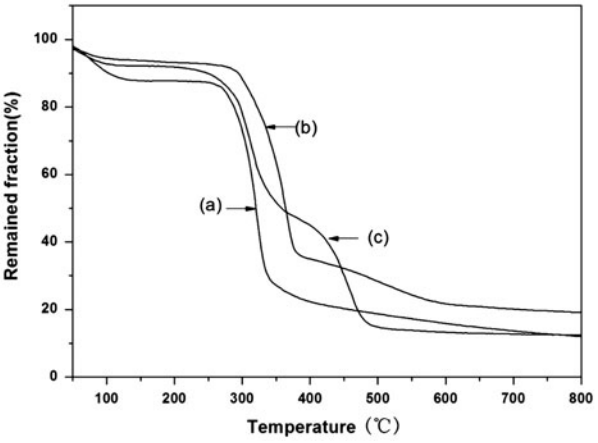

Fig. 3. TGA of of native starch (a), polymer 1 (b) and polymer 2 (c).

The FT-IR spectra of native starch, polymer 1 and polymer 2 are presented in Fig. 2. The band at 3,300, 2,930, 1,640, 1,108, and 980–709 cm^{-1} in Fig. 2(a) were attributable to O–H, C–H, C–C, C–O stretching vibration, and C–H deformations vibration, respectively. Compared with native starch, the band in polymer 1 spectrum at 3,300 was belonging to O–H and N–H stretching vibration, 3,030 cm^{-1} was for Ar–H stretching vibration, 1,596 and 1,540 cm^{-1} were belonging to aromatic C–C stretching vibration, 1,305 cm^{-1} was for the C–N stretching vibration, respectively. The spectra data of polymer 2 also showed presence of O–H and N–H stretching vibration (3,340 cm^{-1}), C–H stretching (2,933 cm^{-1}) and C–C stretching vibration (1,618 cm^{-1}), C–O stretching (1,050 cm^{-1}), and C–H deformations vibration (732, 771 cm^{-1}), respectively.

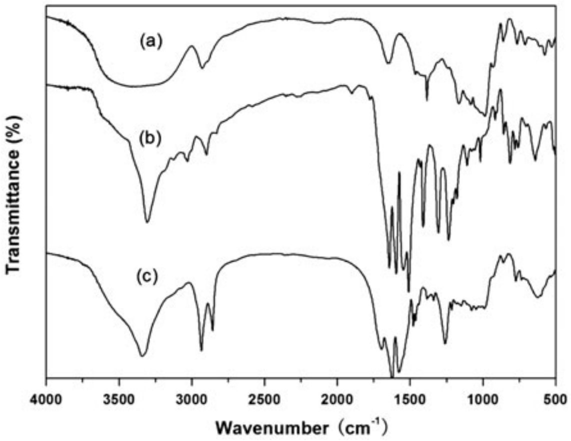

Fig. 2. FT-IR spectra of native starch (a), polymer 1 (b) and polymer 2 (c).

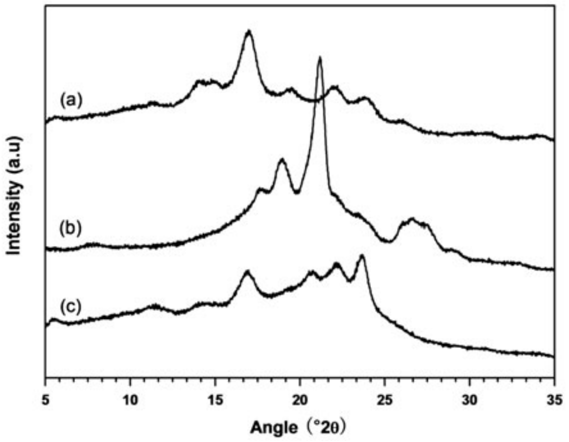

Fig. 4. XRD patterns of native starch (a), polymer 1 (b) and polymer 2 (c).

The TGA was used to examine the changes in thermal stability and to determine the weight loss of the material on heating. The TGA curves for the native starch and cross-linked starch polymers are shown in Fig. 3. The starting temperature of weight loss for native starch was similar as the cross-linked polymers. There was no obvious weight loss until 270°C for native starch, whereas it occurred at 300 and 280°C for polymer 1 and polymer 2. The rates of remained weight for native starch, polymer 1 and polymer 2 at 350°C were 27.09, 62.98, and 51.59%, respectively. This order was consistent with the microstructure of the samples. The crystallization ability of cross-linked starch was higher than that of the native starch [29]. As a result, the thermal stability of cross-linked starch polymers was higher than that of the native starch. On the other hand, it is the cross-linked structure that greatly improved the thermal stability of starch.

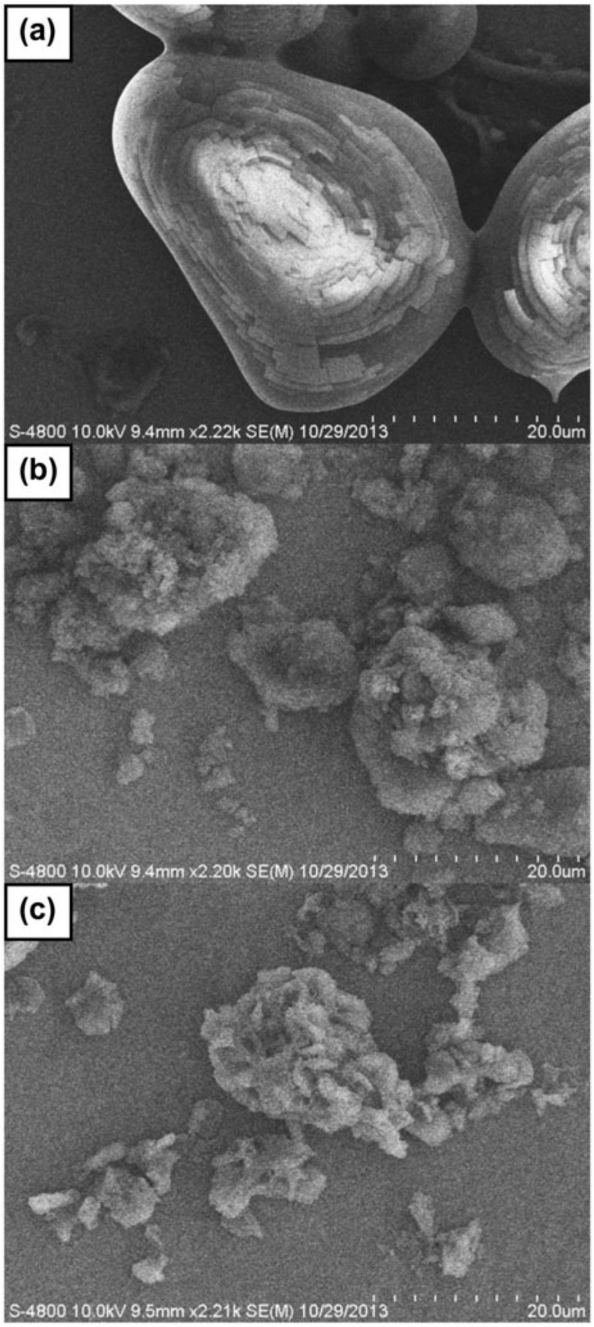

Fig. 5. SEM images of native starch (a), polymer 1 (b) and polymer 2 (c).

XRD measurements were used to check if chemical modification altered the crystallinity of native starch. The XRD spectra of native starch and cross-linked starch polymers are presented in Fig. 4. The native starch showed diffraction peaks at 15.02，16.96, 17.75, 23.04, and 23.70°, which indicated typical crystalline structure of native starch [34]. The polymer 2 showed a similar profile of native starch, which indicated cross-linking with HMDI did not have a major effect on the crystallinity of native starch. However, polymer 1 had new sharp diffraction peaks at 19.01, 22.24 and 26.40°, which implied that the cross-linking process with MDI affected the crystalline structure of native starch.

The SEM images of native starch, polymer 1 and polymer 2, are presented in Fig. 5. The surface of native starch in Fig. 5(a) was found to be globular in shaped with good defined edges. However, the cross-linked starch polymers in Fig. 5(b) and (c) appeared to be lost their smoothness and structural integrity. It was because the orderly crystalline structure of native starch was destroyed and the agglomerations were formed after the cross-linking process.

Table 1 showed the surface area (BET) of the cross-linked starch polymers. The values of BET of cross-linked starch polymers were higher than that of native starch, and the polymer 1 was higher than polymer 2. It is because by introducing different functional groups into the backbone of the original structure, the networks of the starch polymers were changed.

3.2. Sorption studies

Various parameters affecting of nitrophenols adsorption efficiency including types of sorbents, contact time, and solution pH were investigated. Different adsorbents including native starch, polymer 1 and polymer 2 are used for the adsorption of four nitrophenols and the results are shown in Fig. 6. Among the adsorbents, cross-linked polymers were more effective than native starch, and the adsorption

Table 1
The surface area pore characteristics of cross-linked starch polymers

Sample	S_{BET} (mg^2 g^{-1})	S_{BJH} (mg^2 g^{-1})	V_{TOTAL} (cm^3 g^{-1})	V_{BJH} (cm^3 g^{-1})
polymer 1	38.45	36.68	0.142	0.0147
polymer 2	5.26	3.14	0.103	0.0068

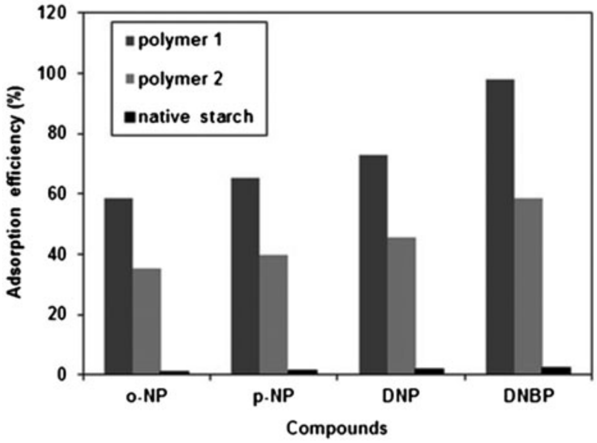

Fig. 6. Comparison of the adsorption efficiency among native starch, polymer 1 and polymer 2 (adsorbents dose 40 mg/30 mL, nitrophenols concentrations: 30 mg L^{-1}, pH 2.5).

efficiency of polymer 1 was much higher than polymer 2 for all the nitrophenols. The reason may be that polymer 1 was highly cross-linked and contained rigid network structure which showed the higher affinity of the guest compounds.

Fig. 7 showed the effect of contact time on adsorption efficiency of the two cross-linked polymers. It was observed that the adsorption efficiency increased fiercely in the first 10 min for the two polymers. Then the trend of the curves reached a plateau, and the maximum adsorption efficiency was obtained after 60 min. The adsorption efficiencies of the four nitrophenols on the two polymers were similar, and increased in the follow: o-NP < p-N*p* < 2,4-DNP < DNBP. The polymers showed highest sorption behaviors to DNBP solution, owing to the superior physical adsorption and hydrogen bonding between the pollutant and the polymers.

The pH of nitrophenols solution is a major parameter in the adsorption process. The effect of pH on the adsorption process was investigated by changing the initial pH of the nitrophenols solution from 2.5 to 11.0. The results are shown in Fig. 8. The adsorption efficiency of all the four nitrophenols decreased with the increase of pH value from 2.5 to 11.0 for the two polymers. As the solutions pH increases, the number of negatively charged site increases and the number of positively charged surface sites decreases. Meanwhile, lower adsorption of nitrophenols at high pH is due to the presence of excess HO$^-$ ions competing with the nitrophenol anions for the adsorption sites. A negatively charged site on the adsorbent does not favor the adsorption of nitrophenol anions due to electrostatic repulsion [12]. The maximum adsorption efficiencies

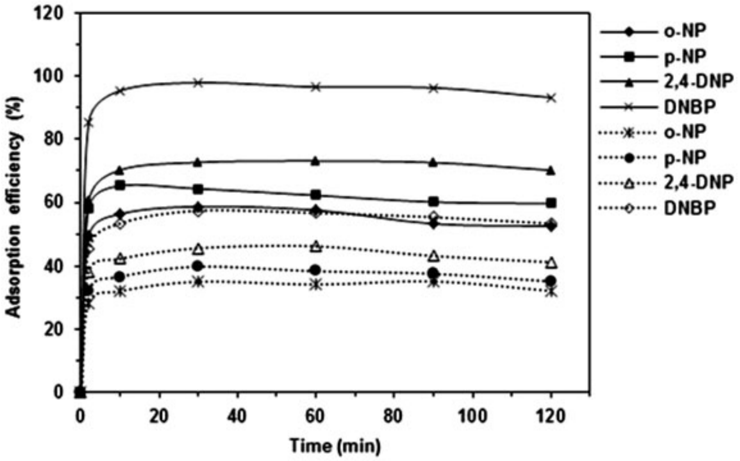

Fig. 7. Effect of contact time on adsorption efficiency of the polymer 1 (solid line) and polymer 2 (dotted line).

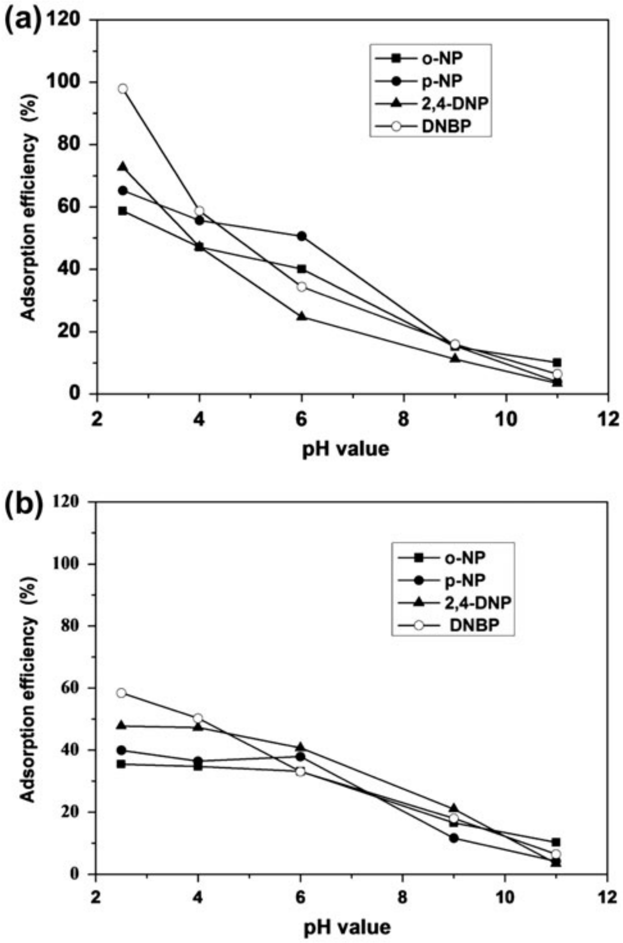

Fig. 8. Effect of the initial pH on the adsorption efficiency for *o*-NP, *p*-NP, 2,4-DNP and DNBP on the polymer 1 (a) and polymer 2 (b).

of o-NP, p-NP, 2,4-DNP, and DNBP solutions were observed at pH 2.5 for the polymer 1, which were 58.7, 65.25, 72.7, and 97.92%, respectively. The polymer 2 also had the highest efficiency at pH 2.5. However, the adsorption efficiencies for the four nitrophenols on the polymer 2 were much lower than that of the polymer 1. Based on above, the polymer 1 prepared by MDI as cross-linking agent was selected for full adsorption studies.

3.3. Adsorption isotherms

In order to determine the adsorption mechanisms of o-NP, p-NP, 2,4-DNP and DNBP solutions onto the cross-linked polymer 1 and to evaluate their relationships with temperatures, Langmuir, Freundlich and Dubinin–Radushkevich isotherm equations were applied to the experimental data. The constant parameters of the isotherm equations for these processes were calculated by regression using the linear forms of isotherm equations. The constant parameters and correlation coefficients (R^2) are summarized in Table 2.

Langmuir and Freundlich models are widely used to describe the equilibrium of an adsorption process between the liquid and solid phases. The Langmuir model is based on assumptions of monolayer, uniform, and finite adsorption site. It also assumes that there is no interaction between molecules adsorbed on neighboring sites. The Freundlich equilibrium model is used for the description of multilayer adsorption with the interaction between adsorbed molecules. The model predicts that the adsorbate concentration on the adsorbent will increase as long as its concentration in the solution increases. The model applies to the adsorption onto heterogeneous surfaces with uniform energy distribution and reversible adsorption. The linear forms of Langmuir and Freundlich isotherms are given by Eqs. (3) and (4), respectively [35,36].

$$\frac{C_e}{q_e} = \frac{1}{(Q_L K_L)} + \frac{C_e}{Q_L} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{4}$$

The R^2 values from the linear regression analyses were low for o-NP and p-NP using the Langmuir equation, indicating that they had poor agreement with this model. The R^2 values for 2,4-DNP and DNBP presented encouraging results, showing a better fit to this model. To determine whether the adsorption process is favorable for the Langmuir type adsorption process, the isotherm can be classified by a term of R_L, a dimensionless constant separation factor. The R_L value of $0 < R_L < 1$ indicated a favorable adsorbate/adsorbent interaction. It is defined as Eq. (5) [37]:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{5}$$

The calculated R_L values are listed in Table 2. They were found in the range of 0.005–0.262 and 0.062–0.546 for 2,4-DNP and DNBP onto cross-linked starch showing favorable adsorption.

The Freundlich isotherm was found to be linear for all the four nitrophenols with high R^2 values. The results in Table 2 showed that the adsorption mechanism followed the Freundlich model better than the Langmuir model based on the R^2 values. The values of K_F and n_F determined from the Freundlich model changed with temperature. The value of n_F for

Table 2
Constant parameters and correlation coefficients calculated for various adsorption models at different temperatures for *o*-NP, *p*-NP, 2,4-DNP and DNBP onto cross-linked starch

	o-NP				*p*-NP				2,4-DNP				DNBP			
Temperature (°)	303	313	323	333	303	313	323	333	303	313	323	333	303	313	323	333
Langmuir equation																
Q_L (mg g^{-1})					8.532	7.589	6.254	5.041	11.501	8.132	6.972	5.435	39.582	36.562	33.378	30.354
K_L (L mg^{-1}) × 10^3					0.238	0.293	0.368	0.453	0.283	0.343	0.546	0.612	0.176	0.256	0.384	0.501
R_L					0.092–0.296	0.078–0.254	0.063–0.213	0.051–0.185	0.123–0.262	0.104–0.226	0.057–0.154	0.005–0.140	0.301–0.546	0.214–0.423	0.145–0.351	0.062–0.231
R^2					0.910	0.798	0.639	0.515	0.956	0.973	0.963	0.939	0.931	0.910	0.888	0.895
Freundlich equation																
K_F (L g^{-1})	0.467	0.285	0.181	0.133	3.914	2.218	1.925	1.254	5.294	4.357	3.503	1.944	22.757	18.354	13.960	9.254
n_F	2.345	2.256	1.925	1.854	2.128	2.056	1.800	1.663	2.867	2.689	2.549	2.384	3.814	3.642	3.483	3.125
R^2	0.981	0.968	0.987	0.995	0.960	0.868	0.932	0.871	0.964	0.989	0.991	0.993	0.983	0.987	0.996	0.946
Dubinin–Radushkevich equation																
Q_{DR} (mg g^{-1})	6.226	5.583	4.762	3.016	9.064	8.469	7.280	5.605	12.356	10.952	10.175	8.732	40.491	38.574	35.687	33.571
E_{DR} (kJ mol^{-1})	0.636	0.527	0.518	0.511	1.801	1.573	1.312	1.266	3.481	2.993	2.495	1.721	5.183	4.568	3.145	2.164
R^2	0.986	0.991	0.996	0.958	0.938	0.986	0.971	0.963	0.969	0.989	0.991	0.926	0.907	0.987	0.948	0.963

Table 3
Thermodynamic parameters for the adsorption of *o*-NP, *p*-NP, 2,4-DNP and DNBP onto cross-linked starch

	Temperature (K)	ln K_D (L g^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	R^2
o-NP	303	0.904	−15.601	−43.674	−2.354	0.982
	313	0.779			−1.923	
	323	0.557			−1.481	
	333	0.356			−1.040	
p-NP	303	1.115	−14.964	−39.859	−2.894	0.979
	313	0.977			−2.492	
	323	0.835			−2.093	
	333	0.564			−1.691	
2,4-DNP	303	2.353	−33.924	−92.531	−5.816	0.989
	313	1.791			−4.925	
	323	1.559			−4.043	
	333	1.141			−3.161	
DNBP	303	3.762	−22.541	−42.642	−9.621	0.985
	313	3.609			−9.194	
	323	3.285			−8.772	
	333	2.970			−8.341	

Freundlich isotherm was found to be greater than 1.0 for all the nitrophenols, indicating the four nitrophenols onto cross-linked starch were favorably adsorbed [38,39]. A higher value of n_F indicated better adsorption and formation of relatively strong bond between the adsorbate and adsorbent [16]. The values of n_F for one kind of nitrophenol were decreased as the increase of the temperature, indicating high temperature was adverse to cross-linked starch adsorption.

The Dubinin–Radushkevich isotherm equation allows the determination of the energy of adsorption and could give additional information about the adsorption mechanism. It is more general than the Langmuir equation because it does not assume a homogeneous surface or constant adsorption potential. It was used to distinguish between the chemical and physical adsorption. The Dubinin–Radushkevich isotherm equation is written as Eq. (6) [40]:

$$\ln q_e = \ln Q_{DR} - \beta\varepsilon^2 \tag{6}$$

The Dubinin–Radushkevich mean free energy E_{DR} (kJ/mol) gives information about the adsorption mechanism and it can be calculated using Eq. (7) [41]:

$$E_{DR} = \frac{1}{\sqrt{2\beta}} \tag{7}$$

If the value of mean free energy E_{DR} is between 8 and 16 kJ/mol, the adsorption process follows the ion-exchange mechanism; if the value of E_{DR} is less than 8 kJ/mol, the nature of adsorption process is physical [41]. The calculated values of E_{DR} calculated based on the experimental data for the four nitrophenols were in the range from 0.518 to 5.18 kJ/mol (Table 2), indicating that the adsorptions of all the four nitrophenols onto the cross-linked starch were physical. With the increase of temperature the value of E_{DR} decreased from 0.636 to 0.511, 9.164 to 5.605, 12.356 to 8.732, and 40.491 to 33.571 kJ/mol for o-NP, p-NP, 2,4-DNP, and DNBP, respectively, so the physical adsorption proceeded to a less extent. The values of Freundlich constant n_F confirmed such an assumption. From analyses of the above models, we drawed conclusions that the favorability of the four nitrophenols onto cross-linked starch increased in the following order: o-NP < p-N*p* < 2,4-DNP < DNBP and high temperature was not beneficial for adsorption.

3.4. Adsorption thermodynamic studies

The thermodynamics for the adsorption of o-NP, p-NP, 2,4-DNP, and DNBP on the cross-linked polymer 1 were investigated in the range of 303–333 K, and the calculated values of the thermodynamic parameters are shown in Table 3. Thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were determined using Eqs. (8)–(10) [42]:

$$K_C = \frac{Q_e}{C_e} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (10)$$

Values of Gibbs free energy ΔG give some information about affinity of adsorbate to adsorbent and driving forces of adsorption. A large negative value of ΔG implies a strong affinity and more spontaneously the adsorption proceeds, spontaneously. The results shown in Table 3 indicated that the values of ΔG became more negative with decreasing temperature, which indicated that the adsorption process was more favorable at low temperatures.

4. Conclusions

In the present study, cross-linked starch-based polymers were synthesized from renewable native starch and used as adsorbents for the adsorption of nitrophenols from aqueous solutions. Results of adsorption experiments showed that the polymer 1 exhibited higher adsorption behaviors than that of polymer 2. The experimental data of the polymer 1 were analyzed according to the Langmuir, Freundlich, and Dubinin–Redushkevich isotherm equations and the Freundlich model appeared to fit the isotherm data better than the Langmuir model. The thermodynamics for the adsorption of four nitrophenols were also investigated and the results showed that Gibbs free energy (ΔG) became more negative with decreasing temperature, which indicated that the adsorption process was more favorable at low temperatures.

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Nomenclature

C_e — equilibrium concentration of solute in the solution (mg L^{-1})
C_o — initial concentration of the solute in the solution (mg L^{-1})
q_e — amount of the adsorbate adsorbed by adsorbent at the equilibrium (mg g^{-1})
V — volume of the solution (L)
W — mass of the cross-linked starch used (g)
Q_L — Langmuir maximum adsorption capacity (mg g^{-1})
K_L — Langmuir equilibrium constant (L mg^{-1})
R_L — Langmuir dimensionless constant (the separation factor)
R^2 — linear correlation coefficient
K_F — Freundlich constant concerned with the relative adsorption capacity (L g^{-1})
n_F — Freundlich constant concerned with the intensity of adsorption
Q_{DR} — Dubinin–Radushkevich saturation capacity (mg g^{-1})
E_{DR} — Dubinin–Radushkevich mean free energy of adsorption (kJ mol^{-1})
ΔG — Gibbs free energy of adsorption (kJ mol^{-1})
ΔH — change of enthalpy (kJ mol^{-1})
ΔS — change of entropy (kJ mol^{-1} k^{-1})
Q_e — amount of adsorbate adsorbed per dm^3 of solution at equilibrium (mg L^{-1})
K_C — thermodynamic distribution constant
T — temperature (K)

Greek symbol

β — constant related to the Dubinin–Radushkevich mean free energy (mol^2 kJ^{-2})
ε — Polanyi potential (J mol^{-1})

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