

Comparison and evaluation of five types of imidazole-modified silica adsorbents for the removal of 2,4-dinitrophenol from water samples with the methyl group at different positions of imidazolium ring

Zhike Wang*, Cunling Ye, Juan Li, Heping Wang, Han Zhang

School of Chemistry and Environmental Science, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, China

HIGHLIGHTS

- Five imidazole-modified silica adsorbents were synthesized.
- The five adsorbents are of primary anion-exchange and electrostatic nature.
- The electrostatic nature was affected by the methyl group of imidazolium ring.
- The five adsorbents are suitable for adsorption of 2,4-DNP with low pK_a value.
- The adsorbent was regenerated and reused ten times by washings with HCl and water.

ARTICLE INFO

Article history:

Received 27 February 2013
Received in revised form 20 June 2013
Accepted 21 June 2013
Available online 1 July 2013

Keywords:

Adsorption
Ionic liquid
Silica
2,4-Dinitrophenol

ABSTRACT

The objective of this work was to improve the understanding the influence of the methyl group at different positions of imidazolium ring on the adsorption behaviors of imidazole-modified silica adsorbents. Five adsorbents named as SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl were synthesized using imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole and 1,2-dimethylimidazole, respectively. These adsorbents were characterized by scanning electron microscope, infrared spectra, thermogravimetric analysis, elemental analysis and BET analysis. Firstly, phenol, 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) were used as adsorbates to investigate the selectivity of SilprImCl and its adsorption capacities followed the order of 2,4-DNP \gg 4-NP $>$ 2-NP \gg 3-NP $>$ phenol. Therefore, 2,4-DNP was used to investigate the adsorption behaviors of the five adsorbents. It was inferred that the adsorbents are of primary anion-exchange and electrostatic nature. The electrostatic nature was affected significantly by the methyl group at different positions of imidazolium ring. The adsorbed amounts of 2,4-DNP decreased in the order of: SilprM₁M₂ImCl \approx SilprM₁ImCl $>$ SilprM₄ImCl $>$ SilprM₂ImCl $>$ SilprImCl. The adsorption–elution experiments indicated that 2,4-DNP can be removed from aqueous solutions by a SilprM₄ImCl packed column and the recovery of 91.6% was obtained. The adsorbent could be regenerated and reused ten times at least by simple washings with HCl and water in turn.

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1. Introduction

Phenolic compounds are main pollutants in surface waters or groundwater and are considered as priority pollutants due to their toxicity and possible accumulation in the environment. Therefore, removal of phenolic pollutants from aqueous solutions is necessary for environment protection and has been investigated

by various physical, chemical and biological methods. A literature review shows that among these methods, adsorption method is very effective and is still constantly investigated and developed due to its low initial cost, simplicity of design and ease of operation [1–4]. Activated carbon [5–12] has been broadly investigated as one of the most effective adsorbents to remove phenolic compounds. However, its application is limited due to its high cost. Research interests into the preparation of novel adsorbents to replace conventional activated carbon have intensified in recent years. Many novel carbonaceous adsorbents such as activated carbon fiber [9,13], activated carbon cloth [14], multi-wall

* Corresponding author. Tel.: +86 373 3325971; fax: +86 373 3326336.
E-mail address: wzk@htu.cn (Z. Wang).

carbon nanotube [15], carbon nanosphere [16], carbon nanoporous adsorbent [17] and a novel carbons prepared from olive stones biomass and novolac resin [18] have been extensively examined. Instead of carbonaceous adsorbents, researcher have worked on other materials such as sawdust [19,20], chitosan [21], MgAl-mixed oxide [22], resin [23,24], polymer [25], bentonite [26–28], manganese nodule leached residue [29] and salicylic acid type adsorbent [30], which have high adsorption capacity for phenolic compounds.

In recent years, ionic liquid-modified silicas, which were prepared by chemically bonding the functionalized ionic liquids on the silica surface, have attracted considerable attention as chromatography stationary phases and solid phase extraction adsorbents [31–33]. Qiu et al. [34] synthesized imidazolium-modified silica with chloride as counter ion, which was successfully used to separate common inorganic anions and some ordinary organic anions. The imidazolium-modified silica has also been used for the separation of alkaloids [35], xylose, glucose [36], lactic acid from fermentation broth [37] and organic acids, amines and aldehydes from atmospheric aerosol sample [38]. N-methylimidazolium-modified silicas with chloride [35–41], tetrafluoroborate [41], bromide [42], hexafluorophosphate [41,43] as counter ions were synthesized, respectively. The other imidazoliums such as 1-butyl-imidazolium [42], 2-ethyl-4-methylimidazole [35–37,44], 3-(propyl-3-sulfonate) imidazolium [38,45] and octylimidazole [46] were also used to modify the silica. Generally, the alkyl chain of ionic liquid-modified silicas between the silica and the imidazolium ring was propyl. However, these ionic liquid-modified silicas including methylimidazolium-modified silica, 1-butyl-imidazolium-modified silica, benzylimidazolium-modified silica and 3-(n-butesulfonate)-imidazolium modified silica were synthesized using octyl as the alkyl chain between the silica and the imidazolium ring [47–51]. Recently, a novel synthetic approach was described, where the 3-mercaptopropyltrimethoxysilane-modified silica was reacted with ionic liquids containing allyl or vinyl as substituents of the imidazolium ring in the presence of azobisisobutyronitrile as the initiator through the radical chain-transfer reaction [52–55]. Another π -complexing sorbents were also prepared by covalently immobilizing ionic liquids onto silica and then coating this silica-supported ionic liquids with silver salts [56,57]. Sun et al. [58] synthesized a novel ionic liquid bonded polysiloxanes with the anion of bis-trifluoromethanesulfonylimide (NTf_2^-) for gas chromatography. As mentioned above, imidazolium-based ionic liquids were usually used for the covalent modification of silica. On the other hand, pyridinium-based ionic liquids were also used to modify silica surface [59,60].

A survey of literatures shows that imidazolium-based ionic liquid-modified silicas exhibit a possibility for removal of anionic compounds from aqueous solutions. However, little is known about the effect of methyl group attached to different positions of imidazolium ring on the adsorption property of imidazole-modified silicas. As far as we know, there is no published work using imidazolium-based ionic liquid covalently modified silicas for the removal of phenolic compounds from aqueous solutions. Based on these considerations, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole and 1,2-dimethylimidazole were used to synthesize the imidazole-modified silica adsorbents, respectively. In this paper, phenolic compounds, phenol, 2-NP, 3-NP, 4-NP, and 2,4-DNP (Fig. 1), with different polarity, aqueous solubility, and pK_a values as adsorbates and the imidazole-modified silicas, SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl, and SilprM₁M₂ImCl (Table 1), as adsorbents were chosen to investigate the adsorption mechanisms. The effects of pH, initial adsorbate concentration, shaking time, adsorbent dosage, temperature, flow rate, elution solvent and sample volume were investigated.

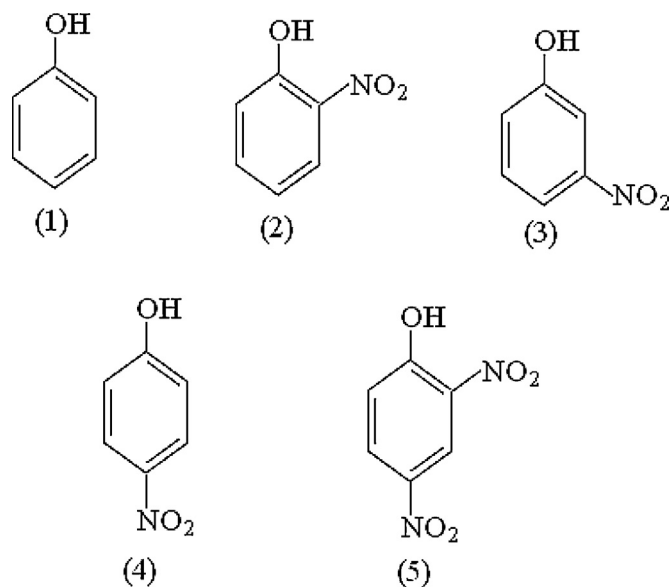


Fig. 1. Chemical structures of phenol (1), 2-NP (2), 3-NP (3), 4-NP (4) and 2,4-DNP (5).

Table 1
Chemical structures of studied adsorbents.

No.	Name	Structure
1	SilprImCl	
2	SilprM ₁ ImCl	
3	SilprM ₂ ImCl	
4	SilprM ₄ ImCl	
5	SilprM ₁ M ₂ ImCl	

2. Experimental

2.1. Materials

Phenol, 2-NP, 3-NP, 4-NP, 2,4-DNP and silica gel (200–300 mesh) were purchased from Sinopharm Chemical Reagent Co., Ltd., while imidazole (99%), 1-methylimidazole (99%), 1,2-dimethylimidazole (99%), 2-methylimidazole (98%), 4-methylimidazole (98%) and 3-chloropropyltriethoxysilane (98%) were obtained from Aladdin Chemistry Co., Ltd. All solvents such as toluene, methanol and ethanol were of analytical grade. Toluene was purified by the following procedure: toluene was firstly dried with calcium chloride, and then was further dried by standing with sodium. Finally, anhydrous toluene was obtained by distillation.

2.2. Preparation of ionic liquid-modified silica

The preparation of imidazole-functionalized silica was the same as described in the literature [37]. In brief, silica was firstly immersed in hydrochloric acid for 24 h and then washed with deionized water and dried at 100 °C for 8 h. The activated silica (6.0 g) was suspended in 60.0 mL of anhydrous toluene and then an excess of 3-chloropropyltriethoxysilane (6.0 mL) was added. Then the suspension was refluxed with stirring for 24 h. The product (chloropropyl silica, SilprCl) was filtered and washed with solvents in the order of toluene, deionized water and methanol. Then the SilprCl was dried at 60 °C for 10 h.

Second, the chemically bonded chloropropyl group on the silica surface was reacted with imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole and 1,2-dimethylimidazole, respectively. In brief, the dry SilprCl (5.0 g) was placed in a reaction flask containing 50.0 mL of anhydrous toluene and a large excess of imidazoles (5.0 g). And then the suspension was refluxed with stirring for 24 h. After refluxing, imidazole-modified silicas were obtained by filtration and washing with toluene, ethanol and methanol in turn and further dry at 60 °C for 10 h. The silica chemically bonded with imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole and 1,2-dimethylimidazole was named as SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl, respectively.

2.3. Characteristic analysis

The surface morphology was examined using the scanning electron microscope (JEOL, JSM-6390 LV) and the FTIR spectra were obtained using a FTIR spectrophotometer (FT-IR NEXUS, Nicolet). After the samples were further dried by freeze dryer (ALPHA 1-2, CHRIST), the thermogravimetric curves were obtained on a thermal analyzer from instruments (Netzsh, STA449C). The carbon, hydrogen and nitrogen of all the intermediates and final materials were determined by elemental analysis that performed on a Vario EL elemental analyzer (Germany). Two parallel analyses were made for each material. Adsorption-desorption isotherms of the synthesized samples were measured on surface area and pore size analyzer (NOVA 1000, Quantachrome Corporation, U.S.). Pore size distributions were evaluated by the BJH method, while surface areas of samples were measured by BET method.

2.4. Adsorption procedure

In order to obtain the equilibrium data and investigate the interactions between adsorbents and adsorbates, the adsorption experiments were investigated in a batch system. The batch system was selected due to its simplicity. 0.1 mol/L HCl and 0.1 mol/L NaOH were used for pH adjustment using a Shanghai pHs-2 pH meter fitted with a combination glass electrode. The solutions containing phenol were added to a series of conical flasks which were shaken at 160 rpm for 5–300 min at constant temperatures (20, 25, 30, 35, 40, 45 °C) to attain equilibrium conditions using a THZ-82(A) thermostatic water-bath shaker (Jintan Scientific Analytical Instrument Co. Ltd., China). A predetermined amount of imidazole-modified silicas were added to the solutions. This was marked as the beginning of the experiment. After shaking, the mixtures were filtrated using filter paper and the phenol concentrations were measured using a UV/visible spectrophotometer (UV-5100, Shanghai Metash Instruments Co., Ltd., China). The amount of adsorbate adsorbed in mmol/g was calculated by the following Eq. (1).

$$q = \frac{V(C_0 - C_t)}{MW} \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the liquid phase concentrations of phenols at initial and at time t , respectively. V (L) is the volume of the solution, M is the molecular weight of corresponding phenol and W (g) is the mass of dry imidazole-modified silicas added.

2.5. Dynamic adsorption, elution and reuse

The dynamic adsorption, elution and reuse were further investigated on the basis of the batch experiments which could predict and optimize separation conditions. SilprM₄ImCl packed cartridges were prepared by empty polypropylene cartridges with the length of 66 mm and an inner diameter of 12.7 mm, which were purchased from Shenzhen Biocomma Biotech Co., Ltd. 250 mg of SilprM₄ImCl was packed into the cartridge using an upper frit and a lower frit to prevent loss of the adsorbent. Then, SilprM₄ImCl packed cartridge was washed with 10 mL methanol and 20 mL de-ionized water in turn. 250 mL of 0.2 mg/L 2,4-DNP aqueous solutions with pH 4.0 were uploaded onto a cartridge at a flow rate of 2 mL/min. After washing with 20 mL de-ionized water, 2,4-DNP was eluted by 4 mL of 0.25 mol/L HCl. After the elution in each case, the adsorbent in the cartridge was washed with 5 mL of the eluting solution and water subsequently. In order to determine the reusability of the ionic liquid-functionalized silica adsorbent, consecutive adsorption–elution cycles were repeated ten times by using the same adsorbent.

3. Results and discussion

3.1. Characterization of adsorbent

The morphological characteristics of silica, activated silica and imidazole-modified silicas were evaluated respectively using a scanning electron microscope (SEM) as shown in Fig. 2. It can be seen from these figures that the surfaces of the imidazole-modified silicas were rougher than that of activated silica, which may be attributed to the surface of activated silica modified by imidazoles.

Infrared spectroscopy has been proven to be a useful tool to identify the chemical modifications [34,38–41]. The spectra of silica, activated silica, SilprCl and imidazole-modified silicas were recorded respectively between 400 and 4000 cm⁻¹ as shown in Fig. 3. It can be seen from the spectra that O–H vibration at 3450 and 1631 cm⁻¹ was attributed to the physical adsorbed water and typical peaks of Si–O–Si could also be observed around 796 and 1090 cm⁻¹. For the silica and the activated silica, the absorption at around 950 cm⁻¹ means the presence of silanol groups (Si–OH) [38]. For the SilprCl, the peak at 950 cm⁻¹ disappeared, which indicated the silanol groups were reacted with 3-chloropropyltriethoxysilane. And the adsorption at 700 cm⁻¹ indicated the presence of C–Cl group. The spectra of imidazole-modified silicas also exhibited the characteristic absorption peaks at 1519 cm⁻¹, 1537 cm⁻¹, 1577 cm⁻¹ and 1591 cm⁻¹ which belong to the finger print region of C–N vibration ranging from 1500 to 1600 cm⁻¹. These results confirmed that imidazoles were successfully bonded on the surface of silica.

The thermogravimetric analysis was obtained for silica, activated silica, SilprCl, SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl in the temperature range of room temperature to 800 °C. Based on the thermogravimetric curves provided in Fig. 4, it can be seen that there is an initial loss of weight at a temperature below 100 °C for all samples. This is attributed exclusively to the removal of adsorbed water molecules. Physically adsorbed water is removed completed by further heating to about 200 °C. For the silica and the activated silica, the mass loss in the region from 200 to 800 °C can be attributed to the condensation of silanol groups [40,42,45,59]. Compared with the silica and the

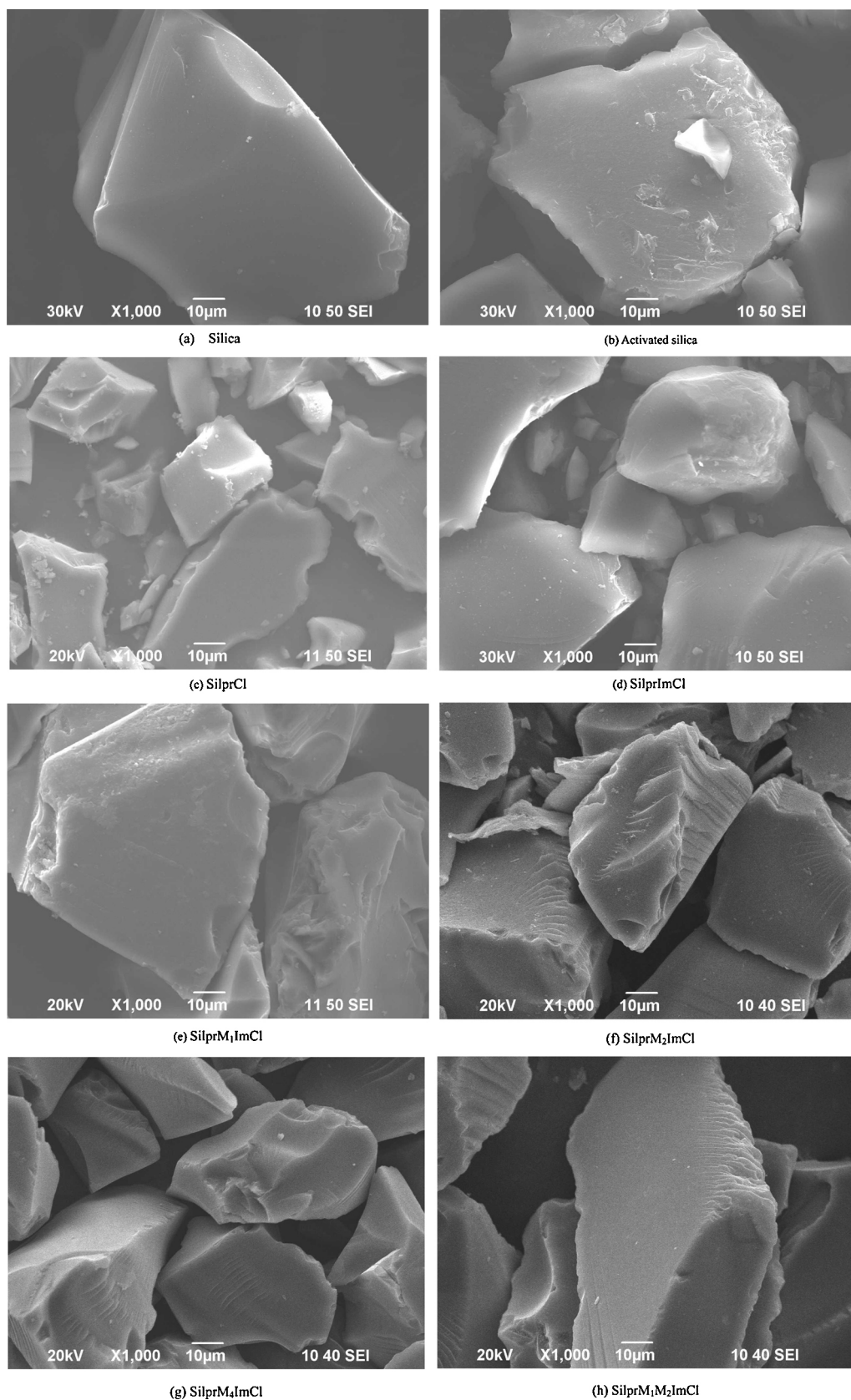


Fig. 2. SEM images of silica (a), activated silica (b), SilprCl (c), SilprImCl (d) and SilprM₁ImCl (e), SilprM₂ImCl (f), SilprM₄ImCl (g) and SilprM₁M₂ImCl (h).

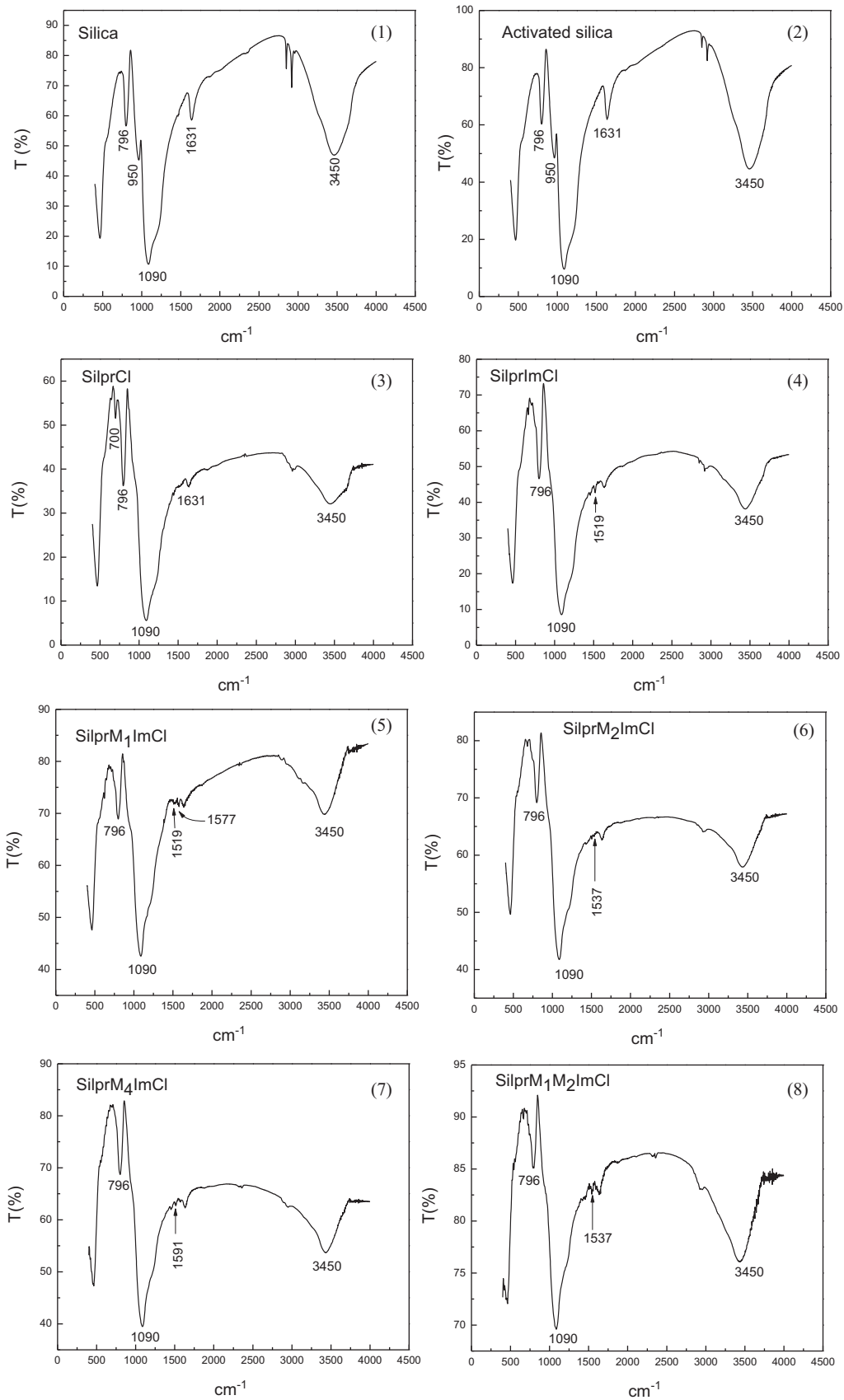


Fig. 3. FTIR spectrum of silica (1), activated silica (2), SilprCl (3), SilprImCl (4), SilprM₁ImCl (5), SilprM₂ImCl (6), SilprM₄ImCl (7) and SilprM₁M₂ImCl (8).

Table 2
Mass loss of SilprCl and imidazole-modified silicas from 200 to 800 °C.

Name	SilprCl	SilprImCl	SilprM ₁ ImCl	SilprM ₂ ImCl	SilprM ₄ ImCl	SilprM ₁ M ₂ ImCl
Mass loss (%)	13.4	15.7	18.6	16.4	17.1	20.3

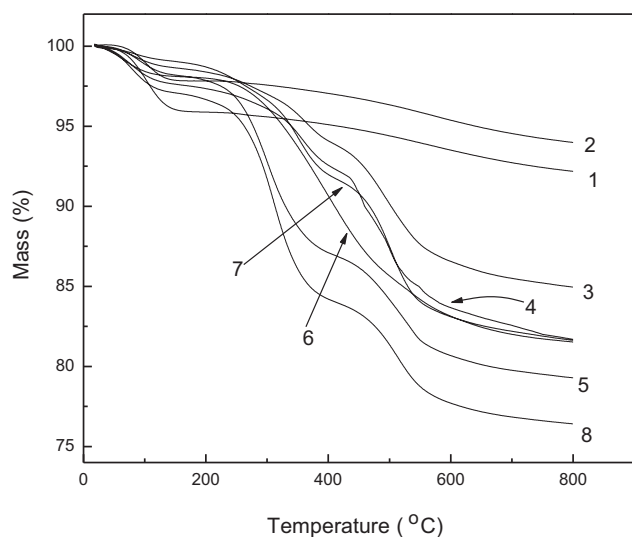


Fig. 4. Thermogravimetric curves obtained for silica (1), activated silica (2), SilprCl (3), SilprImCl (4), SilprM₁ImCl (5), SilprM₂ImCl (6), SilprM₄ImCl (7) and SilprM₁M₂ImCl (8).

activated silica, SilprCl showed a higher mass loss between 200 and 800 °C due to the loss of the chloropropyl moieties attached to the surfaces of silica [45,61]. For the imidazole-modified silicas, the organic content increases again. As shown in Table 2, imidazole-modified silicas presented an even higher mass loss than that of the SilprCl in the temperature range of 200–800 °C. It could be concluded that the ionic liquid was successfully bonded on the surface of silica.

Carbon, hydrogen and nitrogen elemental analyses and the surface coverages of the SilprCl, SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl are presented in Table 3. According to Ref. [45], the surface coverages were calculated according to the following equations:

$$\text{Surface coverage } (\mu\text{mol}/\text{m}^2) = \frac{\%C}{36 \times (1 - \%C - \%H) \times S} \quad (2)$$

$$\text{Surface coverage } (\mu\text{mol}/\text{m}^2) = \frac{\%N}{28 \times (1 - \%C - \%H - \%N) \times S} \quad (3)$$

where %C, %H and %N represent the percentages of carbon, hydrogen and nitrogen, respectively, as determined by elemental analysis shown in Table 3, *S* is the specific surface area of the corresponding silica support (605 m²/g, BET). Surface coverage of SilprCl was calculated according to Eq. (2) based on the percentage amounts of carbon. The surface coverages of SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl were

Table 3
Elemental analysis and surface coverages of SilprCl and imidazole-modified silicas.

Materials	C (%)	H (%)	N (%)	Coverage (μmol/m ²)
SilprCl	6.749	1.716	–	3.39
SilprImCl	8.774	1.770	2.917	1.99
SilprM ₁ ImCl	10.58	2.151	3.198	2.25
SilprM ₂ ImCl	9.873	1.889	2.641	1.82
SilprM ₄ ImCl	10.94	1.986	3.253	2.29
SilprM ₁ M ₂ ImCl	12.12	2.356	3.105	2.22

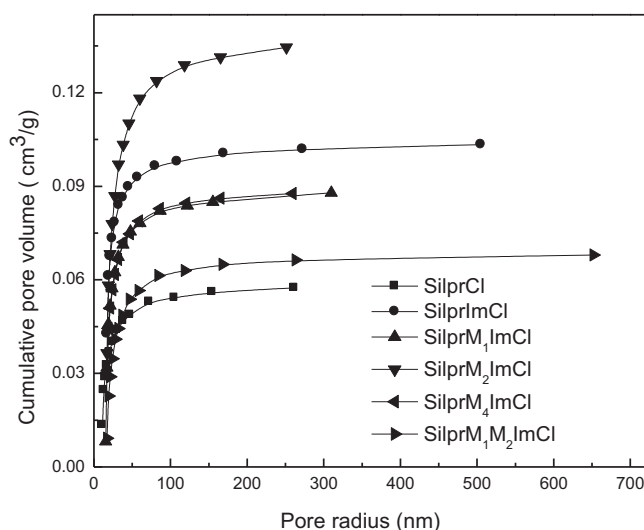


Fig. 5. Pore size distributions of the SilprCl, SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl.

calculated according to Eq. (3) based on the percentage amounts of nitrogen, respectively. The elemental analysis data proved that immobilization on the surface was successful.

Pore size distributions of the SilprCl, SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl are presented in Fig. 5 and associated BET surface area, pore volume and average pore radius values are listed in Table 4.

3.2. Selectivity of adsorbents

In order to investigate the selectivity of the five adsorbents, SilprImCl was selected as adsorbent, and phenol, 2-NP, 3-NP, 4-NP and 2,4-DNP were used as adsorbate, respectively. Previously experimental results showed that phenol was almost not adsorbed onto the SilprImCl at initial concentration 50 mg/L, shaking time 4 h, shaking speed 160 rpm, temperature 30 °C and wide pH range from 2 to 11. Compared with phenol, the substituted phenols demonstrated higher adsorption capacities at initial adsorbate concentration 50 mg/L, shaking speed 160 rpm, shaking time 4 h, temperature 30 °C and pH 4.0, as shown in Fig. 6. It can be concluded that the adsorption of phenolic compounds followed the sequence: 2,4-DNP ≫ 4-NP > 2-NP ≫ 3-NP > phenol. This trend is not consistent with the polarity of these compounds: 4-NP (5.07 D) > 2,4-DNP (3.3 D) > 2-NP (3.14 D) > phenol (1.22 D). Moreover, the aqueous solubility of these compounds also do not match with the

Table 4
Surface areas, pore volumes and average pore radiuses of SilprCl and imidazole-modified silicas.

Materials	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)
SilprCl	261.75	0.06	15.54
SilprImCl	260.13	0.10	15.56
SilprM ₁ ImCl	90.31	0.09	21.94
SilprM ₂ ImCl	218.12	0.13	18.52
SilprM ₄ ImCl	160.93	0.09	17.46
SilprM ₁ M ₂ ImCl	54.75	0.07	25.78

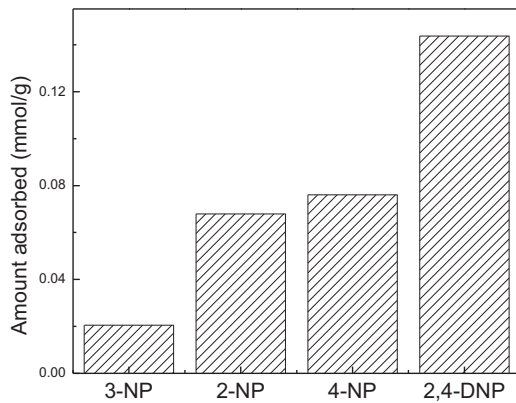


Fig. 6. Selectivity of SilprImCl. Initial adsorbate concentration: 50 mg/L; solution pH: 4.0; shaking speed: 160 rpm; shaking time: 4 h; temperature: 30 °C.

adsorption sequence previously mentioned: phenol (93 g/L) > 2,4-DNP (5.6 g/L) > 2-NP (2.0 g/L) > 4-NP (1.69 g/L) > 3-NP (1.35 g/L). However, the adsorption sequence was opposite to the sequence of the pK_a values of these compounds: 2,4-DNP (3.96) < 4-NP (7.15) < 2-NP (7.17) < 3-NP (8.28) < phenol (9.89). That is to say, SilprImCl showed high adsorption activity toward phenolic compounds with low pK_a value. Based on these results, it is clear that phenolic compounds adsorption onto SilprImCl improved when there is a nitro functional group in the molecule of phenol. This fact could be attributed to the electron-withdrawing effects of nitro functional group added to different positions of phenol, which decreases the electron density of the aromatic rings of the phenolic compounds, decreasing the pK_a values of these compounds. Therefore, 2,4-DNP was used as the adsorbate to further investigate the effect of methyl group attached to different positions of imidazolium ring on the adsorption property of imidazole-modified silicas.

3.3. Effect of pH

The effect of pH on 2,4-DNP adsorption was determined for different pH values ranging from 2.0 to 9.0 at initial concentration 50 mg/L, shaking speed 160 rpm, shaking time 4 h and temperature 30 °C (Fig. 7). It could be seen from this figure that the total amount of adsorption of 2,4-DNP on SilprImCl, SilprM₂ImCl and

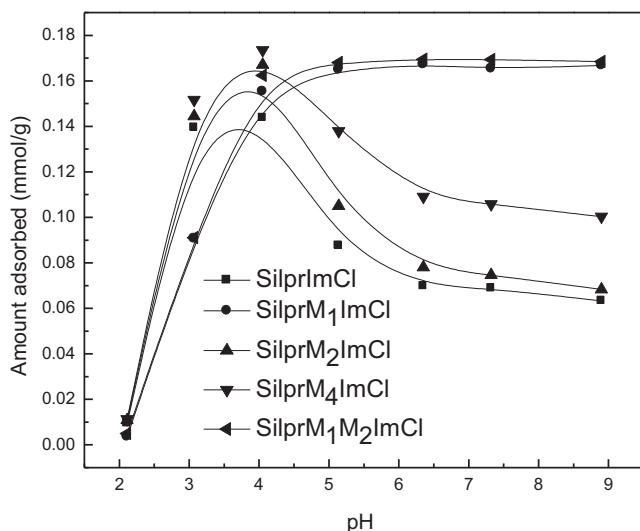
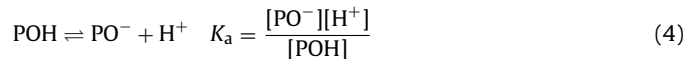


Fig. 7. Effect of pH on the adsorption of 2,4-DNP. Initial concentration: 50 mg/L; shaking speed: 160 rpm; shaking time: 4 h; temperature: 30 °C.

SilprM₄ImCl increases significantly with an increase of pH from 2.0 to 4.0. The adsorption capacity reached a maximum at pH 4.0 and decreased with an increase of pH from 4.0 to 9.0. But for the adsorption of 2,4-DNP on SilprM₁ImCl and SilprM₁M₂ImCl, the total amount of adsorption increases significantly with an increase of pH from 2.0 to 5.0 and maintained a stable value of ca. 0.1684 mmol/g in the pH range of 5.0–9.0. Moreover, over the wide pH conditions ranging from 5.0 to 9.0, the adsorbed amounts of 2,4-DNP on different imidazole-modified silicas decreased in the order of: SilprM₁M₂ImCl ≈ SilprM₁ImCl > SilprM₄ImCl > SilprM₂ImCl > SilprImCl. This trend is not consistent with the sequence of the pK_a values of the alkylimidazoles: 1,2-dimethylimidazole (8.21) > 2-methylimidazole (8.10) > 4-methylimidazole (7.80) > 1-methylimidazole (7.21) > imidazole (6.97) [62].

To explain the effect of pH, we need to clarify the type of interaction between 2,4-DNP and SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl. 2,4-DNP ($pK_a = 3.96$) would act like weak acids in aqueous solutions, the dissociation of hydrogen ion from the 2,4-DNP molecules strongly depends on the pH level of solutions and can be expressed as Eq. (4).



where POH and PO⁻ represent the molecular and dissociated ionic species of 2,4-DNP, respectively and K_a is the dissolution constant of 2,4-DNP. Thus the distribution of PO⁻ can be calculated as a function of solution pH. As shown in Fig. 8, the 2,4-DNP is mainly in molecular form at pH < pK_a and in deprotonated form at pH > pK_a . It is widely recognized that imidazole-modified silicas are anion-exchangeable material. Thus, the total amount of adsorption of 2,4-DNP increases significantly with an increase of pH at pH < pK_a regardless of the types of the adsorbent. According to the above anion-exchange adsorption mechanism, Cl⁻ in solutions would decrease adsorption of 2,4-DNP by the shift of Eqs. (5)–(9) in the left direction.

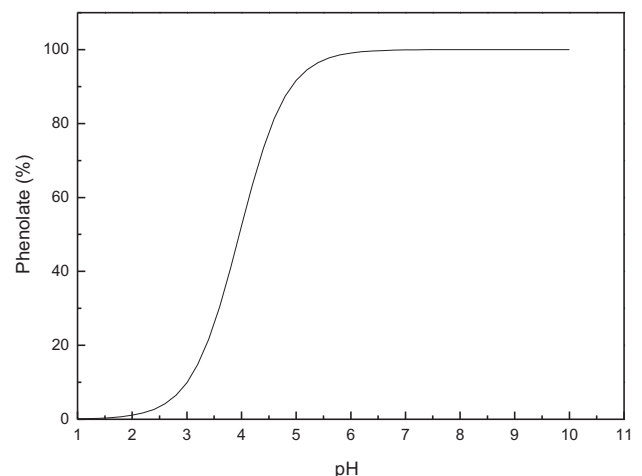
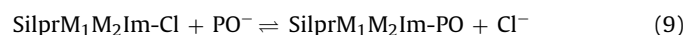
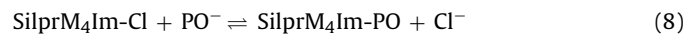
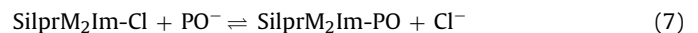
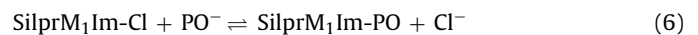
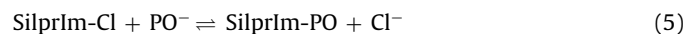


Fig. 8. Effect of pH on anionic form of 2,4-DNP.

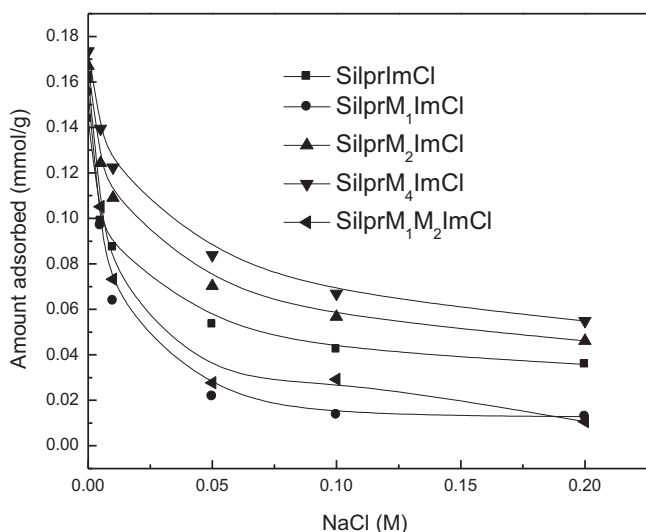


Fig. 9. Effect of NaCl concentration on the adsorption of 2,4-DNP. Initial concentration: 50 mg/L; solution pH: 4.0; shaking speed: 160 rpm; shaking time: 4 h; temperature: 30 °C.

In order to investigate the effect of excess Cl^- concentration on the adsorption of 2,4-DNP, Cl^- ions in the form of NaCl were added into the solutions. As indicated in Fig. 9, the adsorption amount of 2,4-DNP onto imidazole-modified silicas decreases significantly with the NaCl concentration increasing from 0 to 0.2 mol/L. The experimental result was in agreement with the anion-exchange adsorption mechanism. In anion exchange adsorption, it is typical to observe an increase in the adsorption amount of an acidic compound as the pH of the solutions is increased. However, our experimental results suggest that there is other key interaction taking place besides anion-exchange that could be electrostatic in nature. Imidazolium is a large organic cation, phenolate and OH^- ions are attracted simultaneously by the positive imidazolium in basic solutions. Thus, the low adsorption at high pH is probably due to the presence of OH^- ions competing with the phenolate for the residual positively charged adsorption sites on the imidazole-modified silicas surface. The electron density of imidazolium ring should be taken into account for its effect on electrostatic interactions. It is well known that the methyl group, electron-donating group, can strengthen the electron density of imidazolium ring. This could suppress the electrostatic interactions of the imidazolium cation with OH^- ions. Therefore, compared with SilprImCl, SilprM₂ImCl and SilprM₄ImCl have high adsorption capacities for 2,4-DNP in the investigated pH range. As shown in Fig. 7, the differences between the adsorbed amounts of 2,4-DNP on different imidazole-modified silicas may be attributed to the effects that the methyl group was connected at different positions of imidazolium ring. For example, when the methyl group is connected with N of imidazolium ring, the electron density of imidazole ring becomes denser than that of the methyl group on other positions of imidazole ring. This is contributed that N atom of imidazole ring is more electronegative than C atom of imidazole ring. The electron-withdrawing inductive effect of N atom could further reduce electrostatic interactions because of weakening the positive imidazolium. Therefore, for SilprM₁ImCl and SilprM₁M₂ImCl, this could be the reason that the total amount of adsorption maintained a stable value in the pH range of 5.0–9.0.

3.4. Effect of initial concentration and adsorbent dosage

The effect of initial 2,4-DNP concentration on adsorption capacity on the five adsorbents was investigated at pH 4.0, shaking

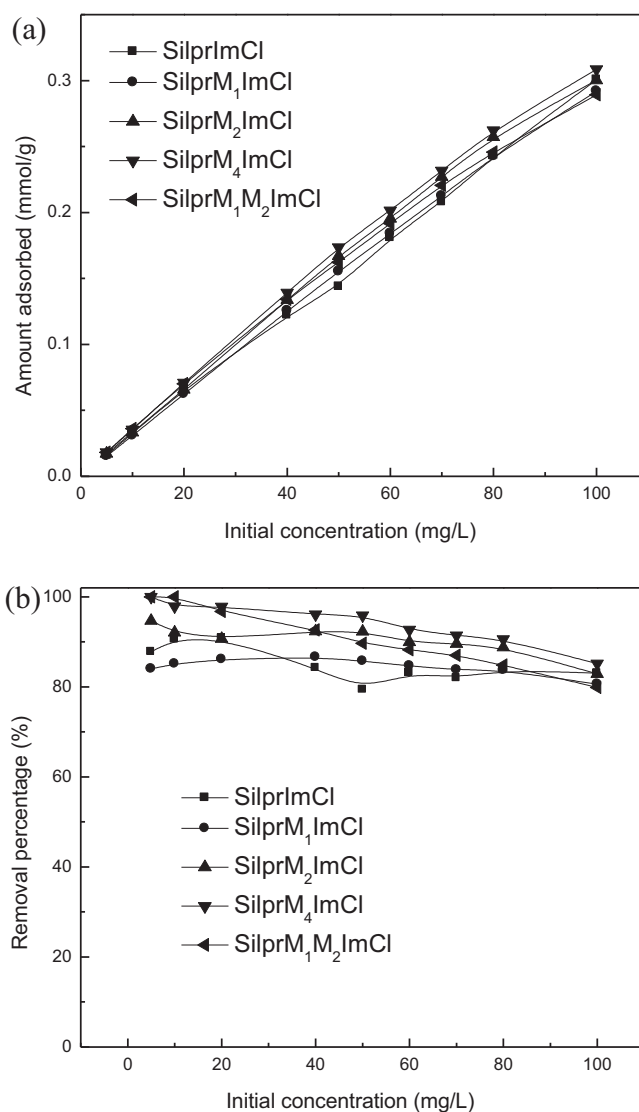


Fig. 10. Effect of initial concentration on the adsorption of 2,4-DNP. Solution pH: 4.0; shaking speed: 160 rpm; shaking time: 4 h; temperature: 30 °C.

speed 160 rpm, shaking time 4 h, temperature 30 °C. As shown in Fig. 10(a), the adsorption capacity increased sharply with the increasing of initial concentration of 2,4-DNP from 5 to 100 mg/L. This can be attributed to the increase in the mass-transfer driving force due to the increase of initial concentration. It is evident from Fig. 10(b) that the high removal percentage was obtained for the five adsorbents even the initial concentration was increased from 5 to 100 mg/L. The influence of dosage of the five adsorbents was investigated at different dosages ranging from 10 to 80 mg, while other variables were kept constant. As illustrated in Fig. 11, the amount of 2,4-DNP adsorbed per unit mass of adsorbent decreases with increasing of adsorbent dosages. This could be explained as follows: increasing adsorbent dosage will provide larger surface area, the concentration of initial 2,4-DNP was fixed. Hence, the adsorbent was excessive with the further increasing of adsorbent dosage. On the other hand, the low adsorption of 2,4-DNP with much adsorbent dosage is possibly due to raising pH accompanied with excessive adsorbent dosage for SilprImCl, SilprM₂ImCl and SilprM₄ImCl [63].

In order to further elucidate the interaction of 2,4-DNP with adsorbents, the adsorption isotherm models of Freundlich and Langmuir, which were shown in the linearized form of Eqs. (10)

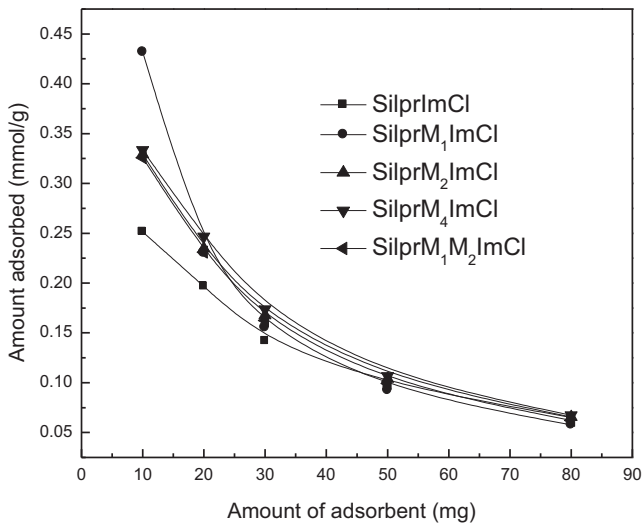


Fig. 11. Effect of amount of adsorbent on the adsorption of 2,4-DNP. Initial concentration: 50 mg/L; solution pH: 4.0; shaking speed: 160 rpm; shaking time: 4 h; temperature: 30 °C.

and (11), respectively, were used to evaluate the adsorption experimental data provided from Fig. 10.

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (10)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \frac{1}{C_e} \quad (11)$$

where k_f and $1/n$ are the constant indicative of the relative adsorption capacity of the adsorbent and the constant indicative of the heterogeneity factor of Freundlich adsorption isotherm, respectively. q_m and b are the monolayer adsorption capacity (mmol/g) and the constant related to the free energy of adsorption of Langmuir, respectively. q_e and C_e are the equilibrium adsorption capacity (mmol/g) and the equilibrium concentration (mg/L), respectively.

According to the analysis results, the experimental data are described by Langmuir model better than by Freundlich model. The calculated values of the Langmuir and Freundlich constants and the correlation coefficients are presented in Table 5. Since the intercept of the Langmuir for SilprM₁ImCl adsorbent was smaller than zero, the q_m and b were not given.

3.5. Effect of shaking time

The influence of shaking time on 2,4-DNP adsorption from aqueous solutions was given in Fig. 12 at initial concentration 50 mg/L, solution pH 4.0, shaking speed 160 rpm and temperature 30 °C using SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl as adsorbent, respectively. In order to further investigate the mechanism of adsorption of 2,4-DNP on the five adsorbents, the kinetic data shown in Fig. 12 were statistically investigated using the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models, respectively. It was demonstrated that the rate of adsorption fits the pseudo-second order expression as shown in Eq. (12) quite well.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (12)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mmol/g) and k is the rate constant of the pseudo-second order adsorption (g/mmol min).

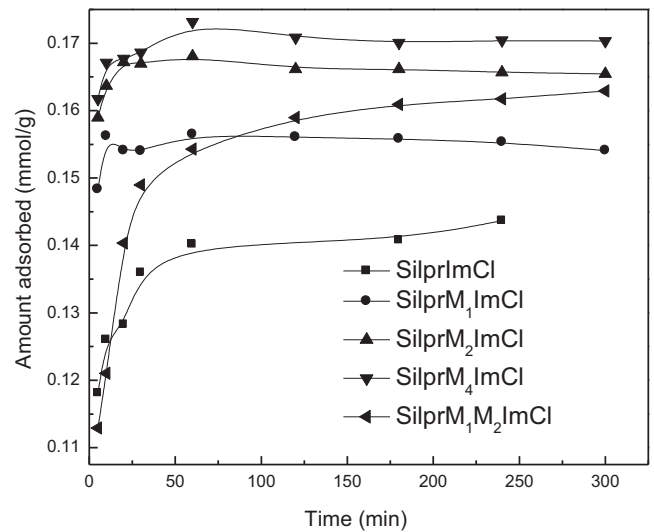


Fig. 12. Effect of shaking time on the adsorption of 2,4-DNP. Initial concentration: 50 mg/L; solution pH: 4.0; shaking speed: 160 rpm; temperature: 30 °C.

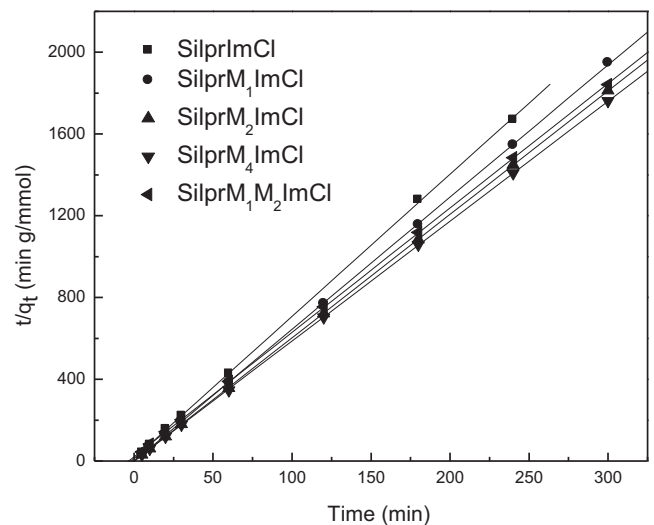


Fig. 13. Pseudo-second order kinetics of 2,4-DNP adsorption on five adsorbents. Conditions are same as Fig. 12.

Eq. (12) reveals that there must be linear relation between t/q_t and t . When Eq. (12) was applied to the data shown in Fig. 12, the t/q_t versus t for different adsorbents was drawn in Fig. 13. As can be seen from the figure, the plots of t/q_t versus time are straight, with a correlation coefficient (R^2) higher than 0.9998. The values of q_e and k for five adsorbents can be calculated from the slopes and intercepts of these pseudo-second order kinetic plots by using Eq. (12). When $t \rightarrow 0$, h can be defined as the initial adsorption rate, hence:

$$h = kq_e^2 \quad (13)$$

Table 6 presents the values of the correlation coefficients, the rate constant, the equilibrium adsorption capacity and the initial adsorption rate.

3.6. Effect of temperature

Experiments were also conducted to investigate the effect of temperature on 2,4-DNP adsorption from aqueous solutions. The temperatures used were 20, 25, 30, 35, 40 and 45 °C, the other

Table 5
Langmuir and Freundlich isotherm constants.

Adsorbents	Langmuir constants			Freundlich		
	q_m (mmol/g)	b (L/mg)	R^2	k_f (mmol/g)(mg/L) ⁿ	1/n	R^2
SilprImCl	0.7955	0.0368	0.9653	0.0303	1.2870	0.9669
SilprM ₁ ImCl	–	–	0.9959	0.0216	1.0557	0.9863
SilprM ₂ ImCl	0.2704	0.2443	0.9707	0.0471	1.3212	0.9693
SilprM ₄ ImCl	0.3028	0.6375	0.9965	0.0972	2.0243	0.9567
SilprM ₁ M ₂ ImCl	0.2459	0.5999	0.9611	0.0844	2.3821	0.9971

Table 6
Parameters for the adsorption of 2,4-DNP on five adsorbents calculated by the pseudo-second order kinetic model.

Adsorbents	q_e (mmol/g)	k (g/mmol min)	h (mmol/g min)	R^2
SilprImCl	0.144	3.958	0.082	0.99984
SilprM ₁ ImCl	0.155	23.95	0.574	0.99994
SilprM ₂ ImCl	0.166	24.78	0.681	0.99998
SilprM ₄ ImCl	0.171	126.4	3.675	0.99998
SilprM ₁ M ₂ ImCl	0.164	1.823	0.049	0.99996

variables were kept constant. As shown in Fig. 14, the adsorption capacity rose with the decrease of the temperature, indicating the apparent exothermic nature of the entire process. Similar effect has been reported by other authors [7,12,19,21]. It may be concluded that the low temperature is favorable for the adsorption process.

3.7. Comparison with other adsorbents

A comparison between the adsorption capacities of 2,4-DNP onto the SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl, SilprM₁M₂ImCl and other adsorbents are listed in Table 7. It can be concluded that the five types of adsorbents have been used to remove 2,4-DNP from aqueous solutions as effectively as the other adsorbents reported in the literatures.

According to above discussions, the five adsorbents are of primary anion-exchange and electrostatic nature. The methyl group at different positions of imidazolium ring affected significantly the adsorption behaviors of 2,4-DNP onto the imidazole-modified silica adsorbents. The adsorption capacities of 2,4-DNP onto the SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl at initial concentration 50 mg/L, pH 4.0, adsorbent dosage 30 mg, shaking speed 160 rpm, shaking time 4 h,

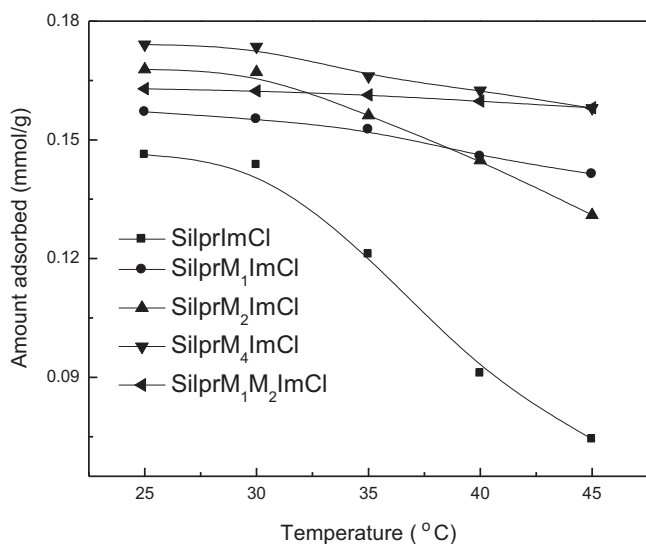
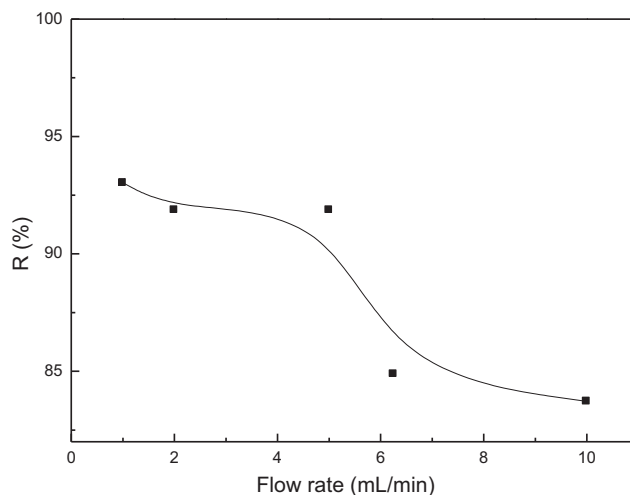
Table 7
Comparison of adsorption capacities of 2,4-DNP onto SilprImCl, SilprM₁ImCl, SilprM₂ImCl, SilprM₄ImCl and SilprM₁M₂ImCl with different adsorbents.

Adsorbents	Initial concentration (mmol/L)	Adsorption capacity (mmol/g)	Reference
AP-55 (activated carbons from apricot stone shells)	0.326	1.521	[6]
Granular activated carbon	0.326	0.179	[6]
Charcoal activated powder	0.326	1.016	[6]
Activated carbon fibers	–	2.272	[13]
Carbon nanospheres	1.086	0.178	[16]
Yellow bentonite	0.082	0.054	[27]
MIP-SiO ₂	1.901	0.085	[64]
Olive wood	–	0.032	[65]
Cotton cellulose C2	0.2	0.061	[66]
SilprImCl	0.326	0.181	This study
SilprM ₁ ImCl	0.326	0.184	This study
SilprM ₂ ImCl	0.326	0.195	This study
SilprM ₄ ImCl	0.326	0.201	This study
SilprM ₁ M ₂ ImCl	0.326	0.192	This study

temperature 30 °C are 0.144, 0.155, 0.167, 0.174 and 0.162 mmol/g, respectively.

3.8. Dynamic adsorption, elution and reuse

SilprM₄ImCl has higher adsorption capacity and rate at optimized conditions, judging from Figs. 12 and 13. So it was selected as adsorbent in the dynamic adsorption experiments. The influence of flow rate of sample solutions was investigated under the optimum conditions by passing 250 mL of 0.2 mg/L 2,4-DNP sample solutions with pH 4.0 through the cartridge. The flow rates were adjusted in a range of 1–10 mL/min. As shown in Fig. 15, it was found that the recovery was practically not changed up to

**Fig. 14.** Effect of temperature on the adsorption of 2,4-DNP. Initial concentration: 50 mg/L; solution pH: 4.0; shaking speed: 160 rpm; shaking time: 4 h.**Fig. 15.** Effect of sample flow rate on the recovery of 2,4-DNP. 250 mg of SilprM₄ImCl, sample volume 250 mL, concentration 0.2 mg/L, pH 4.0 and temperature 25 °C.

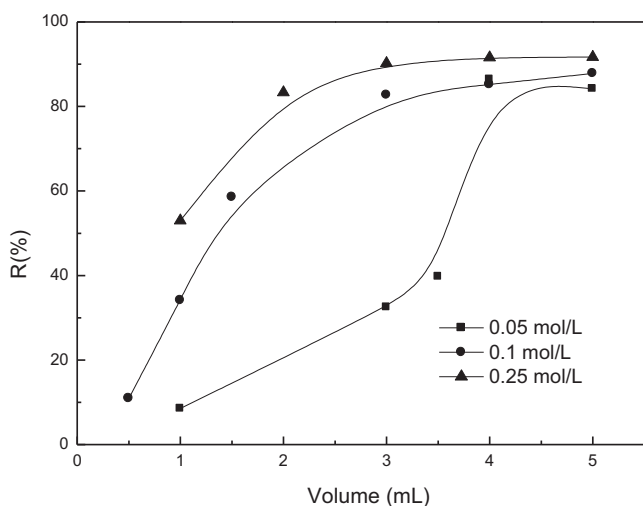


Fig. 16. Effect of concentrations and volumes of HCl on the recovery of 2,4-DNP. 250 mg of SilprM₄ImCl, sample volume 250 mL, concentration 0.2 mg/L, pH 4.0 and temperature 25 °C.

5 mL/min. The recovery decreased significantly when the flow rate is over 5 mL/min. Thus, the flow rate of 2 mL/min was preferred to subsequent work. The elution condition was investigated by using various concentrations and volumes of HCl for the desorption of retained 2,4-DNP. As shown in Fig. 16, the recovery of 2,4-DNP increased with the increase of the concentration and volume of HCl, respectively. The maximum quantitative recovery (91.6%) was obtained with 4 mL of 0.25 mol/L HCl. So, 4 mL of 0.25 mol/L HCl was recommended as eluent in further experiments. In order to obtain high pre-concentration factor, the effect of sample volume on the recovery was investigated in the range of 50–500 mL containing 50 µg of 2,4-DNP. The results are presented in Fig. 17. From this figure, it can be seen that the maximum sample volume could be up to 500 mL with the recovery >91%. In the present study, a high pre-concentration factor of 125 was obtained because 4 mL of 0.25 mol/L HCl was used as eluent in these experiments. The stability and potential regeneration of the column were also investigated. When the adsorbed 2,4-DNP was eluted, the column packed with SilprM₄ImCl can be reused after washing with 10 mL methanol and 20 mL de-ionized water, respectively. The recovery of 2,4-DNP within at least 10 adsorption–elution cycles did not

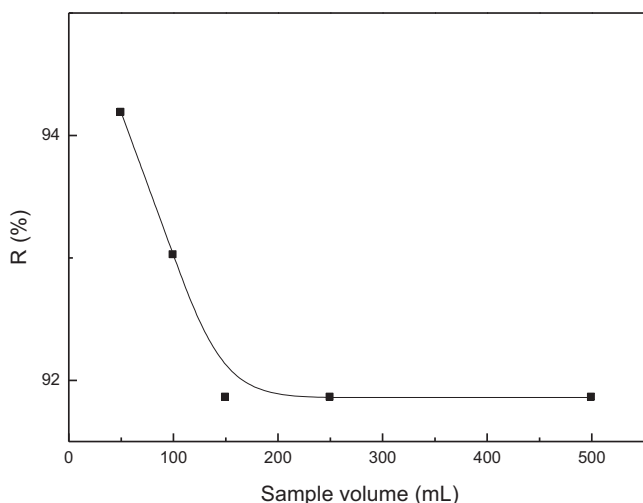


Fig. 17. Effect of sample volume on the recovery of 50 µg 2,4-DNP. 250 mg of SilprM₄ImCl, pH 4.0 and temperature 25 °C.

decrease significantly, which indicated that this sorbent possesses stable characteristics.

Previous optimization indicated that 250 mL of 0.2 mg/L 2,4-DNP sample solutions with pH 4.0 were loaded onto a SilprM₄ImCl-packed cartridge at the flow rate of 2 mL/min. The recovery was more than 91% when 4 mL of 0.25 mol/L HCl was used as eluent. And the adsorbent could be regenerated and reused ten times at least.

4. Conclusions

The five types of adsorbents are of primary anion-exchange and electrostatic nature, which show high adsorption activity toward phenolic compounds with low pK_a value. Moreover, the electrostatic nature was affected significantly by the methyl group at different positions of imidazolium ring. Over the wide pH conditions ranging from 5.0 to 9.0, the adsorbed amounts of 2,4-DNP decreased in the order of: SilprM₁M₂ImCl \approx SilprM₁ImCl > SilprM₄ImCl > SilprM₂ImCl > SilprImCl. The pseudo-second order kinetic model gives satisfactory fitting. The adsorbent could be regenerated and reused ten times at least by simple washings with HCl and water in turn. It is reasonable to say that the recommended imidazole-modified silica adsorbents for the removal and recovery of 2,4-DNP from aqueous solutions are feasible in technique. Though ionic liquid-modified silicas are growing promptly mainly due to the adjustable nature of both cation and anion, their potential application as adsorbents might be limited because of the high price of ionic liquids. When production on a mass scale will start the price of ionic liquids is expected to drop significantly, which would promote the applications of ionic liquid-modified silica adsorbents. It should also be pointed out that the limited pH stability of silica might be the potential drawback of this method. Further work is underway in our laboratory to exploit novel ionic liquid-modified silica adsorbents for the removal and recovery of phenolic compounds from aqueous solutions by adjusting the nature of ionic liquids.

Acknowledgements

The financial support provided by National Natural Science Foundation of China (21107022), the Science and Technology Department (Nos. 102300410097 and 122300410271), the Education Department of Henan Province of China (No. 2010GGJS-067) and Innovation Scientists and Technicians Troop Construction Projects of Henan Province are gratefully acknowledged.

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