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Novel thiourea-modified magnetic ion-imprinted chitosan/TiO₂ composite for simultaneous removal of cadmium and 2,4-dichlorophenol

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ABSTRACT

In the present study, a novel type of adsorbent called thiourea-modified magnetic ion-imprinted chitosan/TiO₂ (MICT) was prepared with the purpose of improving its feature as a composite adsorbent. The simultaneous cadmium ion adsorption and 2,4-dichlorophenol (2,4-DCP) degradation by this novel composite adsorbent were investigated. The obtained results showed that the optimum pH values for adsorption of cadmium and degradation of 2,4-DCP were approximately 6.0–7.0. The kinetics study demonstrated that the adsorption process proceeded according to the pseudo-second-order model. The maximum adsorption capacity for cadmium was 256.41 mg/g according to the Langmuir model. The intermediate products of the reaction consisted of 4-chlorophenol, 1,4-benzoquinone, phenol, cyclohexanol, and some other trace substances, as identified by gas chromatography/mass spectroscopy (GC/MS) technique. The sequential degradation process was proposed, including reductive dechlorination or reaction with hydroxyl radicals based on the products identified. The used sorbent was reusable after regenerated through desorption, and the adsorption and degradation capacities were barely affected after five cycles.

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1. Introduction

The co-contamination of aquatic systems with heavy metal ions and toxic organic pollutants is a problem of global concern [1]. Heavy metals and aromatic compounds from industrial activities, such as plating, metallurgy, and dyeing, are a threat to humans and to the environment due to their toxicity and persistence after they are released into the natural environment [2]. Among these pollutants, cadmium has attracted the attention of environmentalists as one of the most toxic heavy metals [3]. Some aromatic compounds, such as 2,4-DCP can provoke disturbances in the structure of cellular bilayer phospholipids, which may cause carcinogenic and mutagenic effects [4]. Many traditional methods applied to remove the two kinds of pollutants, such as electrochemical precipitation, ion exchange, reverse osmosis and solvent extraction, are mainly based on applications in single systems containing either metal ions or organic solutes [5]. Moreover, these conventional separation techniques have many disadvantages for example; the high cost, possible production of secondary toxic compounds and the

generation of sludge leading to high disposal costs [6,7]. Adsorption has been recognized as one of the most popular and effective methods for the removal of the above-mentioned pollutants from wastewaters due to the flexibility in design and operation offered by the adsorption process [8]. However, this process is expensive, so low-cost biosorbents have been given increasing attention as they can significantly reduce the cost of an adsorption system [9].

Chitosan and chitin are the most important materials examined for removal of toxic metal ions owing to their inexpensive and effective in nature [10]. Chitosan is hydrophilic, biodegradable, harmless to living things, and offers ease of chemical derivatization. Moreover, chitosan has many amino and hydroxyl groups that can chelate heavy metals. Therefore, chitosan is a very promising material for chelating resins [11,12]. However, its flaws, such as weak mechanical strength, dissolution in acidic solutions, and leaching of organics like carbohydrates, are serious when raw chitosan is used. These drawbacks have hindered the applications for treatment of waste metallic streams [12,13].

In recent years, various efforts have been focused on the stability of chitosan, which is a potential way to overcome the disadvantages. Chitosan is often crosslinked to confer better microbiological and mechanical resistance [14]. Crosslinking agents like glutaraldehyde, epichlorohydrin, triphosphate, and ethyleneglycol diglycidylether have been used to stabilize chitosan in acid solutions [11–15]. However, the metal uptake efficiency of crosslinked

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chitosan is reportedly often much lower than that of raw chitosan. The functional groups on chitosan for metal binding are involved in the crosslinking reaction; thus, the sorption decreases. In the present study, an innovative ion-imprint technology was developed with the objective of achieving higher sorption capacity of resin and stability. The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. Thus, efforts in the current research were directed towards modification with chelating functionalities to improve the adsorption capacity.

Adsorption capacity was improved extensively through the above process. For organic pollutants removal, a novel approach to achieve this purpose is developing photo-oxidation via an advanced oxidation process (AOP). AOPs have been proven to be an effective treatment method for the degradation of toxic organic pollutants from wastewaters [16]. In this application, TiO_2 is a benchmark photocatalyst because of its various merits, such as chemical stability, high photocatalytic activity, and non-toxicity. TiO_2 has an excellent ability to degrade numerous kinds of organic pollutants in water into harmless end-products of CO_2 , H_2O , and some simple mineral acids [17].

The topic of TiO_2 coupled with chitosan was studied by some researchers in recent years. For example, Qian et al. [18] prepared a novel bactericidal and mildew-proof fabric through immobilization of TiO_2 -chitosan composite on cotton fibers, which exhibits high bactericidal ratios for *Escherichia coli*, *Staphylococcus aureus* and *Aspergillus niger* under visible light irradiation. In the wastewater-purification area, TiO_2 and chitosan were also taken together to synthesize microporous materials for the arsenic, Ni^{2+} adsorption and methyl, reactive dyes removal [19–21]. However, there were many drawbacks existed in these researches, for example; a single treatment object, low removal efficiency, difficult for separation and recycle. In light of the foregoing, the current study presents the combined effect of photodegradation-adsorption using the prepared chitosan/ TiO_2 composite under the illumination of UV light as a new method for the treatment of heavy metal and organic co-contaminating wastewater. Efforts were directed towards overcome the above drawbacks to improve its feature.

Separating the adsorbents from the reaction solution is a problem after adsorption. Traditional separation methods, such as filtration and sedimentation, are ineffective due to the small size and low density of the adsorbents. Magnetic separation technology is a much better solution. Magnetic carriers are used as support material that can be easily separated from the reaction medium and stabilized in a fluidized bed reactor by applying a magnetic field [11,22,23].

In the present work, a novel type of adsorbent, namely, thiourea-modified magnetic ion-imprinted chitosan/ TiO_2 composite (MICT), was prepared for the purpose of improving separation, adsorption, and degradation capacities. Molecular imprinting technology and photodegradation technology were coupled through the immobilization of nanometer TiO_2 and Fe_3O_4 on ion-imprinted chitosan matrixes during the synthesis. The multiple functions of the composite were investigated.

2. Materials and methods

2.1. Chemicals

Chitosan (degree of deacetylation: 92%) was purchased from Haidebei Ocean Biology Co. (Jinan, China). Analytical pure 2,4-DCP purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) was used in the preparation of solution for the tests. All other inorganic chemicals of analytical grade were purchased from Shanghai First Reagent Co., China.

2.2. Preparation of solution

A stock solution containing 2.0 g/L Cd(II) was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in ultrapure water. The exact concentration of the stock solution was determined by flame atomic absorption spectrometry (PerkinElmer AA700, USA). A stock solution of 2,4-DCP was prepared by dissolving 0.5 g 2,4-DCP in 1.0 L ultra-pure water. The 2,4-DCP solution was stored in a brown glass bottle to avoid photodegradation. Test solutions were prepared by diluting the stock solutions to the desired concentrations. The pH value of the solution in the present study (2.0–8.0) was adjusted to the required value using 0.1 mol/L NaOH or HNO_3 solutions.

2.3. Preparation of MICT

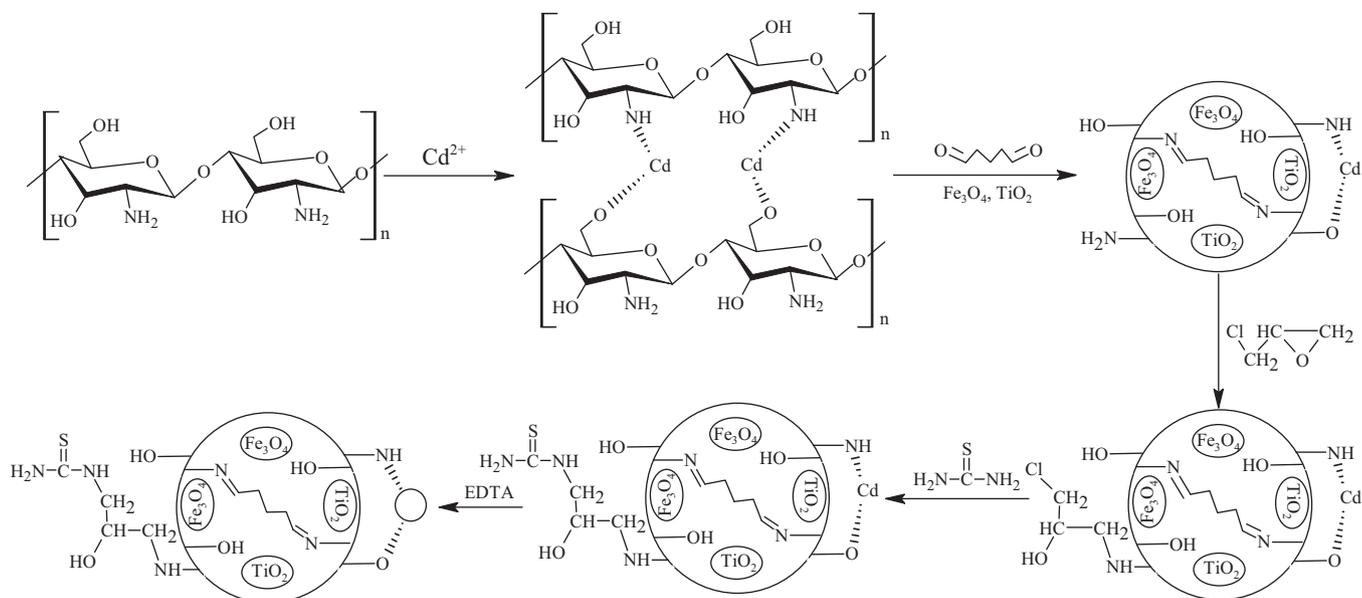
Fe_3O_4 nanoparticles were prepared by co-precipitating Fe^{2+} and Fe^{3+} ions by ammonia solution and treating them under hydrothermal conditions. The process was improved according to the reported method [24]. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M iron ions. Chemical precipitation was achieved at 80 °C under vigorous stirring by the addition of NH_4OH solution (25%, w/v). During the reaction process, the pH was maintained at about 10.0. The precipitates were heated at 80 °C for 1 h, washed several times with distilled water and ethanol, and finally dried at 60 °C.

Chitosan (2.5 g) was dissolved in acetic acid (2.5%, v/v) and then added into a 500 mL beaker containing 50 mL cadmium nitrate solution (initial concentration: 2.0 g/L). The mixed solution was stirred continuously at 60 °C for 6 h, after which 1.0 g TiO_2 and 1.25 g Fe_3O_4 nanoparticles were added during the stirring process. Then, 0.5 mL glutaraldehyde solution was added to the mixture to form gel. After completion of the reaction, the pH in the system was adjusted to 9.0 using 2 mol/L NaOH. The mixture was stirred and heated on a water bath for 3 h at 60 °C. The magnetic chitosan/ TiO_2 beads were formed and washed with acetone and distilled water.

Grafting of sulfur groups using epichlorohydrin as a crosslinking agent was carried out similar to the procedure described by Zhou et al. [25] with chitosan flakes. Four milliliters of epichlorohydrin was dissolved in 100 mL acetone. The obtained magnetic chitosan/ TiO_2 microspheres were added, and the slurry was mixed at 60 °C for 5 h. Up to 5 g thiourea (dissolved in 100 mL distilled water) was then added. Stirring was continued for 5 h at 60 °C. The collected resin was washed with acetone and distilled water. Subsequently, the resin was put into a beaker containing 100 mL 0.1 mol/L EDTA and stirred for 12 h at 25 °C. This process was repeated until no cadmium ions were detected in the solution. The resin was treated with 0.1 mol/L NaOH for 2 h and then washed several times with distilled water and acetone in turn. The MICT resin was obtained after drying at 60 °C overnight. The preparation process is presented in Scheme 1. To determine the effect of imprinted cadmium ion and modification on the improvement of cadmium sorption, two other sorbents were prepared as follows: (i) a modified but non-imprinted (MCT) sorbent prepared according to the above approach without the cadmium ion; and (ii) cadmium ion-imprinted chitosan/ TiO_2 (ICT) sorbent prepared without modification by thiourea.

2.4. Characterization of the resin

Photographs were taken using a scanning electron microscope (SEM) (FEI QUANTA-200, Holland FEI Company, Holland) to analyze the morphology and surface structure of the adsorbents. Fourier transform-infrared (FT-IR) spectra were used to identify the structure of the synthesized resin. The FT-IR spectra were obtained using an FT-IR spectrophotometer (WQF-410, Beijing, China). The



Scheme 1. Prepared procedure of MICT adsorbent.

sample was prepared mixing 1 mg of the material with 100 mg of spectroscopy-grade KBr.

2.5. Adsorption and degradation experiments

All experiments were conducted at $25 \pm 0.1^\circ\text{C}$. In the pH effect experiment, 0.05 g adsorbent was added into a 200 mL total solution containing Cd(II) (50 mg/L) and 2,4-DCP solution (10 mg/L) at various initial pH (2.0–8.0). The mixture was shaken in a reciprocal shaker (120 rpm) for 6 h. An ultraviolet lamp (20 W, 0.5 m long, and 0.02 m in diameter) was available in the shaker and placed at a distance of 10 cm above the vessel.

For the kinetics experimental study, 0.05 g MICT sorbent was added to 200 mL cadmium ion solution with initial concentrations of 50, 100, and 200 mg/L at pH 7.0. The 2,4-DCP concentration was adjusted to 10 mg/L. The mixture was shaken at 120 rpm. The samples were taken at different time intervals and analyzed for the residual cadmium concentrations.

In the sorption isotherm study, 0.05 g MICT sorbent was added to 200 mL cadmium solution with different initial concentrations (20, 50, 80, 100, 140, 180, and 200 mg/L). The solution pH and 2,4-DCP concentration in the solution were adjusted to the same value as the above experiments. Other procedures were the same as those described in the experiment on pH effect.

2.6. Desorption experiments

Up to 200 mL cadmium solution with a concentration of 50 mg/L and 0.05 g MICT composite sorbent were mixed for 6 h at pH 7.0. The agitation rate was fixed at 120 rpm. The cadmium-loaded sorbent was then separated from the solution and washed with ultrapure water to remove any unadsorbed cadmium ion. The cadmium-loaded sorbent was subsequently agitated with 100 mL of 0.1 mol/L EDTA. The final concentration of cadmium ions in the aqueous phase was determined by an atomic absorption spectrophotometer. The desorption ratio of cadmium ions from MICT was calculated from the amount of metal ions adsorbed on MICT and the final concentration of cadmium ions in the desorption medium. The desorbed adsorbents were then treated with 0.1 mol/L NaOH to neutralize the hydrogen ions that adhered onto the adsorbent surface.

The regenerated sorbent was used in the subsequent sorption-desorption experiments.

2.7. Analytical methods

The pH value during the experiment was measured with a 210 FE20 laboratory pH meter (FE20 Mettler Toledo, Shanghai, China). The initial and residual concentrations of cadmium were determined using an atomic absorption spectrometer (Perkin-Elmer Analyst 700 AAS, USA). The 2,4-DCP concentration in the aqueous solution was determined using a UV-visible spectrophotometer (Model UV-2550, Shimadzu Company, Tokyo, Japan) at 306 nm [26]. The amounts of cadmium and 2,4-DCP removed were calculated by the differences between the initial concentrations of cadmium and the added 2,4-DCP and the final concentrations of cadmium and 2,4-DCP in the filtrate. All data were analyzed using Origin 8.0 software or mapped with Sigmaplot 10.0. The reported error bars for obtained data represent one standard error of the arithmetic mean.

2.8. GC/MS analysis

The intermediates and end-products of 2,4-DCP after photodegradation were identified by GC/MS on a Shimadzu QP-2010 Ultra instrument equipped with RTX-5 capillary column (30 m \times 0.25 mm) according to the method described by Parshetti and Doong [27] with minor modification. The column temperature was initially set at 45°C for 1 min, increased to 280°C at a rate of $24^\circ\text{C min}^{-1}$, and held at that temperature for 1 min. Helium at a flow rate of 1 mL min^{-1} was used as the carrier gas, injector temperature was maintained at 250°C . The transfer line and ion trap manifold were set at 280°C and 230°C , respectively. The mass range scanned was from 45 amu to 550 amu under full-scan acquisition mode. The samples used for GC/MS spectrometry analysis were prepared according to the following procedure. The reaction suspension was first centrifuged at 10,000 rpm for 20 min. The reaction products in the supernatant were acidified to pH 2.0–3.0 followed by extraction with dichloromethane. One gram anhydrous Na_2SO_4 was added to the extract to remove trace amounts of water, and then concentrated to about 1 mL on a rotary evaporator.

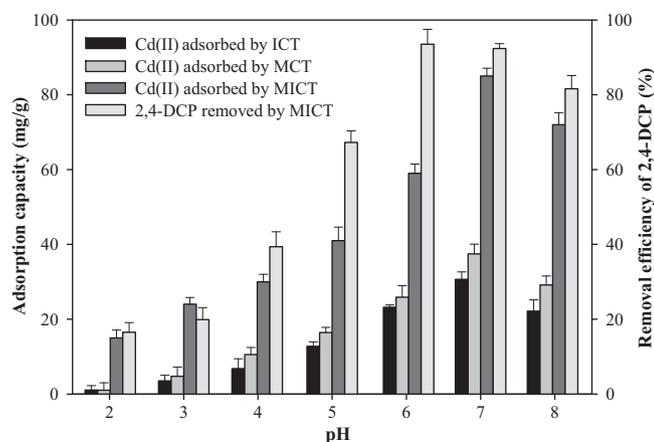


Fig. 1. Effect of pH on Cd(II) and 2,4-DCP removal by the prepared adsorbents.

3. Results and discussion

3.1. Effect of pH

Metal ion and organic material adsorption on both non-specific and specific adsorbents is pH-dependent [28,29]. The pH of the medium affects the solubility of metal ions and the surface characteristics of sorbents [30]. The effects of the initial pH on cadmium removal and 2,4-DCP degradation at pH 2.0–8.0 are shown in Fig. 1. Studies beyond pH 8.0 were not attempted as the precipitation of the ions as hydroxides would have likely occurred [31]. As shown in Fig. 1, the adsorption capacities by ICT and MCT at various pH values tested were much lower than those of MICT. The higher adsorption capacity of Cd(II) by MICT compared with that of ICT or MCT imply that the application of ion-imprinted technology and thiourea modification are relative to the improvement of the adsorption capacity of MICT. The adsorbed cadmium by MICT increased when the solution pH increased from 2.0 to 7.0 and reached the maximum value of 85.6 mg/g at pH 7.0. However, an opposite result was obtained with further increase in pH. Little Cd(II) was removed when the solution was adjusted to pH 2.0. The pH dependency of removal efficiency could be explained by the functional groups involved in the metal uptake. At low pH values, the protons of amino and hydroxyl functional groups are very difficult to dissociate, which increases the protonation of these groups on the surface. On the other hand, a large number of H^+ and H_3O^+ in the solution competed with Cd(II) for the adsorption sites [32]. When the pH values increased, the negatively charged density on the cell surface increased because of the deprotonation of the metal-binding sites. Therefore, the uptake of metal ions (positive charge) increased. When the pH is higher than 7.0, the OH^- in the system and the functional groups on the surface of the cell wall compete for heavy metal ions, which decrease biosorption capacity [33,34]. Similar results were obtained with the adsorption of cadmium from aqueous solution by chitosan [35].

The optimum pH for 2,4-DCP removal was found at pH 6.0–7.0. The removal efficiency decreased when the pH was higher or lower than this condition. The whole reaction process of 2,4-DCP removal can be divided into two stages. In the first stage, 2,4-DCP in the solution was adsorbed onto the sorbent's surface. Then, the degradation process occurred. The effects of adsorption and photodegradation on 2,4-DCP removal were presented in Fig. S1 and discussed in the support information. The 2,4-DCP concentration in the solution decreased quickly in the first stage due to the fast adsorption rate. However, this process was seriously influenced by the solution pH. The 2,4-DCP ($pK_a = 7.98$) is neutral and un-ionized at acidic conditions and is negatively charged when $pH > 7.98$. The point of

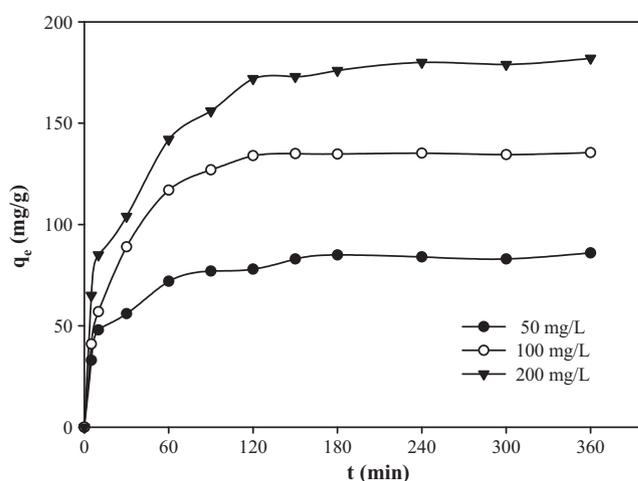


Fig. 2. Effect of time on the Cd(II) adsorbed by MICT.

zero charge for TiO_2 is between pH 5.6 and 6.4 [36]. The surfaces of the adsorbents were much more easily protonated at low pH and could form electrostatic repulsion to prevent the adsorption of 2,4-DCP from the solution. When the pH was very high, the adsorbents and 2,4-DCP were negatively charged and dispelled each other. The adsorption reaction was also difficult to carry out. Thus, both acidic and alkaline conditions were not beneficial to 2,4-DCP adsorption, as they resulted in decreased degradation. Whereas the optimum pH was around 7.0 for cadmium sorption and 2,4-DCP degradation by MICT, a pH value of 7.0 was implemented in subsequent experiments.

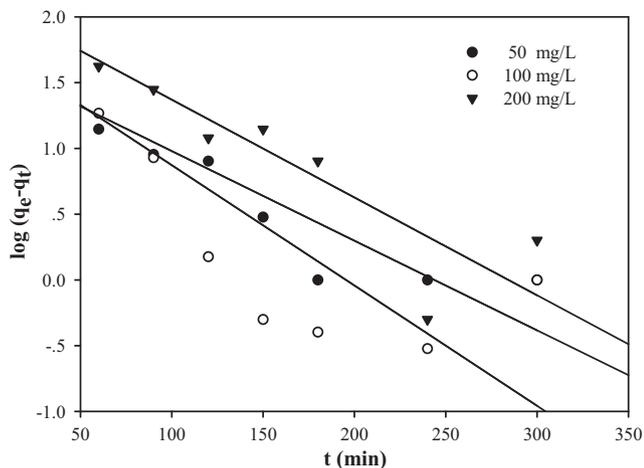
3.2. Adsorption kinetics

Equilibrium time is an important parameter to heavy metal wastewater treatment process. Cd(II) removal by adsorption as a function of contact time with different initial concentrations (50, 100, and 200 mg/L) is shown in Fig. 2. MICT exhibited good adsorptive performance during the first 120 min. There was little increase of cadmium adsorption with contact time beyond 120 min. These results demonstrated that the actual adsorption of metal ion binding to the adsorbent was very rapid.

To investigate the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, two kinetic models including pseudo-first and pseudo-second orders have been exploited to analyze the experimental data [37]. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions in the solid phase [14]. The linearized form of the two models for the sorption of Cd(II) ions onto MICT at various initial concentrations is given in Figs. 3 and 4. The kinetic parameters are presented in Table 1. The validity of each model is checked by comparing the R^2 values. Accordingly, as shown in Table 1, the adsorption of Cd(II) on the resin perfectly fits the pseudo-second order model well. High correlation coefficients are obtained ($R^2 > 0.998$) when the pseudo-second order model is employed for all concentrations and the calculated equilibrium adsorption capacity is close to the experimental data. The first-order kinetic process has been used for reversible reactions with an equilibrium established between the liquid and solid phases. On the other hand, the pseudo-second order kinetic model assumes that the rate-limiting step may be chemical adsorption [37]. In this case, the adsorption behavior of Cd(II) implies that the adsorption rate may be controlled by intraparticle diffusion [38–40]. Similar results were obtained when some chitosan derivatives were used as adsorbents for Cd(II) adsorption from the solution [9,40,41].

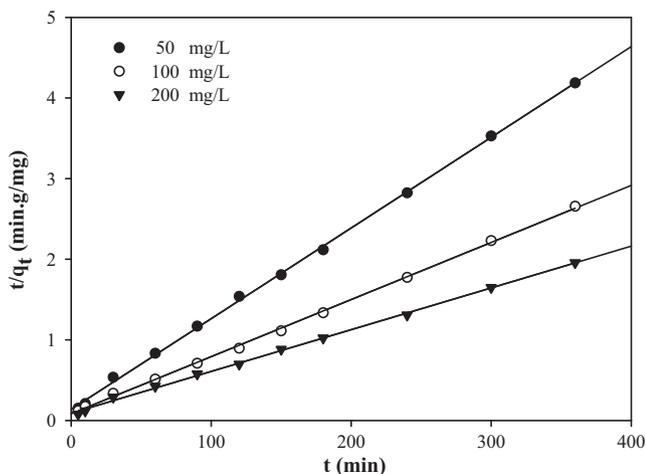
Table 1
Kinetic parameters for adsorption of Cd(II) on MICT.

C_0 (mg/L)	Pseudo-first-order			Pseudo-second-order			
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	h (mg/g min)	R^2
50	0.016	45.85	0.910	9.08×10^{-4}	89.29	7.24	0.999
100	0.021	61.29	0.793	6.04×10^{-4}	140.85	11.99	0.999
200	0.017	129.90	0.896	2.99×10^{-4}	192.31	11.04	0.998

**Fig. 3.** Pseudo-first-order kinetic plots for the adsorption of Cd(II) onto MICT resin at various initial concentrations.

3.3. Effect of initial cadmium concentration and isotherms studies

Based on the previous analysis, the optimal pH values in the isotherm experiment of Cd(II) removal on the biosorbents were controlled at 7.0. The initial cadmium concentrations in the sorption isotherm experiments were controlled at a range of 20 mg/L to 200 mg/L. As shown in Fig. 5, the amounts of cadmium adsorbed increase with initial cadmium concentration in the solution. This phenomenon could be attributed to the fact that the initial cadmium concentration was the driving force for overcoming the mass transfer limitation between the adsorbents and the fluid phase. A high initial concentration of cadmium enhanced the mass transfer driving force; thus, adsorption capacity increased. In addition, an elevated initial cadmium concentration increased the number of collisions between the adsorbate and adsorbent, which also enhanced the adsorption process [42–44].

**Fig. 4.** Pseudo-second-order kinetic plots for the adsorption of Cd(II) onto MICT resin at various initial concentrations.

The 2,4-DCP degradation efficiency was very high (>84%) even under very low cadmium concentration, and further increased (up to 98%) with initial cadmium concentration. This result was probably due to the increased uptake of cadmium with increase in initial cadmium concentration. The adsorbed cadmium may combine with =S on the surface of MICT, forming Cd–S–R complex or CdS nanoparticles, which is beneficial to the degradation of organic contents. Similar results were obtained using crosslinked chitosan nano-CdS to degrade Congo Red [45] and CdS-sensitized TiO₂ in phenazopyridine photodegradation [46].

The cadmium sorption data were fitted using Langmuir equation (Fig. S2). The Langmuir equation can well describe the sorption isothermal behavior with high correlation coefficients ($R^2 = 0.994$). The maximum cadmium sorption capacity (Q_{max}) of MICT was 256.41 mg/g at 25 °C. To our best knowledge, the sorption capacities of chitosan are normally low except for a few chitosan derivatives (e.g., crosslinked chitosan/PVA beads and chitosan-based crab shells) [40,49]. The sorption capacity of MICT for Cd(II) was compared with that of several adsorbents as reported in the literature (Table 2). The sorption capacity of MICT for Cd(II) in the current study was the highest among these sorbents, indicating that the thiourea-modified ion-imprinted composite sorbent developed in the current study has a great potential for the treatment of heavy metal wastewater.

3.4. SEM-EDX and FT-IR analysis

The SEM micrographs of the resin are presented in Fig. 6A and B. The images illustrate that the surface of the MITC particles was loose, rough, and marked with holes and tiny interspaced structures, which increase the contact area and improve metal ion adsorption. The energy dispersive X-ray (EDX) analysis spectrum of the resin is shown in Figs. 6C and D. Comparing the EDX spectrum before and after adsorption, there is an obvious peak of cadmium in the EDX spectrum after adsorption, which demonstrates that cadmium was adsorbed on the resin.

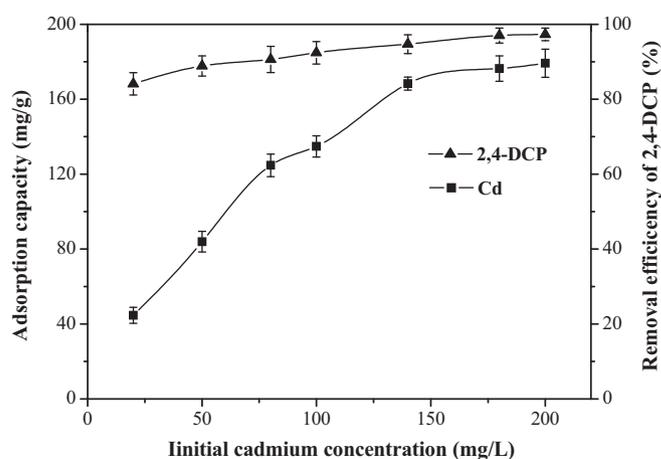
**Fig. 5.** Effect of initial cadmium concentration on cadmium removal and 2,4-DCP degradation by MICT.

Table 2
Comparison of maximum sorption capacities of various sorbents for Cd(II) obtained by Langmuir adsorption model.

Sorbents	Sorption conditions		Q_m (mg/g)	Reference
	pH	T (°C)		
MICT	7.0	25	256.41	This study
Chitosan	7.0	25	6.07	[35]
Crosslinked chitosan/PVA beads	6.0	30	106.4	[40]
Chitosan crosslinked with ECH-TTP	7.0	25	83.75	[9]
Chitosan loaded with Reactive Orange 16	8.5	20	89.92	[47]
Immobilized chitosan	7.0	25	50.58	[48]
Chitosan-based crab shells	8.0	23	105	[49]
Chitosan-based hydrogels	4.5–5.5	25	135.51	[58]

The functional groups and surface properties of the resins were confirmed by the FT-IR spectra shown in Fig. 7. The adsorption band around 3400 cm^{-1} reveals the stretching vibration of the N–H group bonded with the O–H group in chitosan. The peaks at around 1650 cm^{-1} confirms the N–H scissoring from the primary amine due to the free amino groups in the crosslinked chitosan [14,50]. The bands at 1595 , 1377 , and 1076 cm^{-1} are related to N=O vibrations, C–O stretching vibrations, and O–H stretching, respectively. The peak at 1155 cm^{-1} represents the N–C=S group. The increasing intensity at 3388 , 3365 , and 1076 cm^{-1} in the spectra of ICT and MICT indicate that the amine groups and the hydroxyl groups on chitosan were protected by ion-imprint technology during the crosslinking process. Another change in the spectrum was N–C=S. A new peak (1155 cm^{-1}) appeared in the spectra of MCT and MICT compared with that of ICT. This finding was probably because the MCT and MICT resins were modified by thiourea, which provided the N–C=S group. The bands at 560 – 660 cm^{-1} are associated with the metal –O stretching vibration. Combining the results of the

FT-IR spectrograph with the pH effect, a conclusion can be drawn, namely, the amino and hydroxyl groups are the major functional groups involved in cadmium bonding. A coordination complex was probably formed between chitosan and cadmium with the participation of the –NH₂ and –OH functional groups.

3.5. Degradation of 2,4-DCP

The degradation pathway depends on the kind of catalyst and reaction condition in the system. The degradation pathways of 2,4-DCP by visible-light responsive photocatalysis have been discussed in previous works [51,52], in which the reductive dechlorination was proposed as the major decomposition route. Several intermediates, including 2-chlorophenol, 4-chlorophenol, phenol, and chlorocatechol, have been detected [27,36]. To evaluate the reaction pathways of 2,4-DCP by MICT in the current study, GC/MS was used to identify the intermediates and end-products. The GC/MS results revealed the presence of several intermediate compounds,

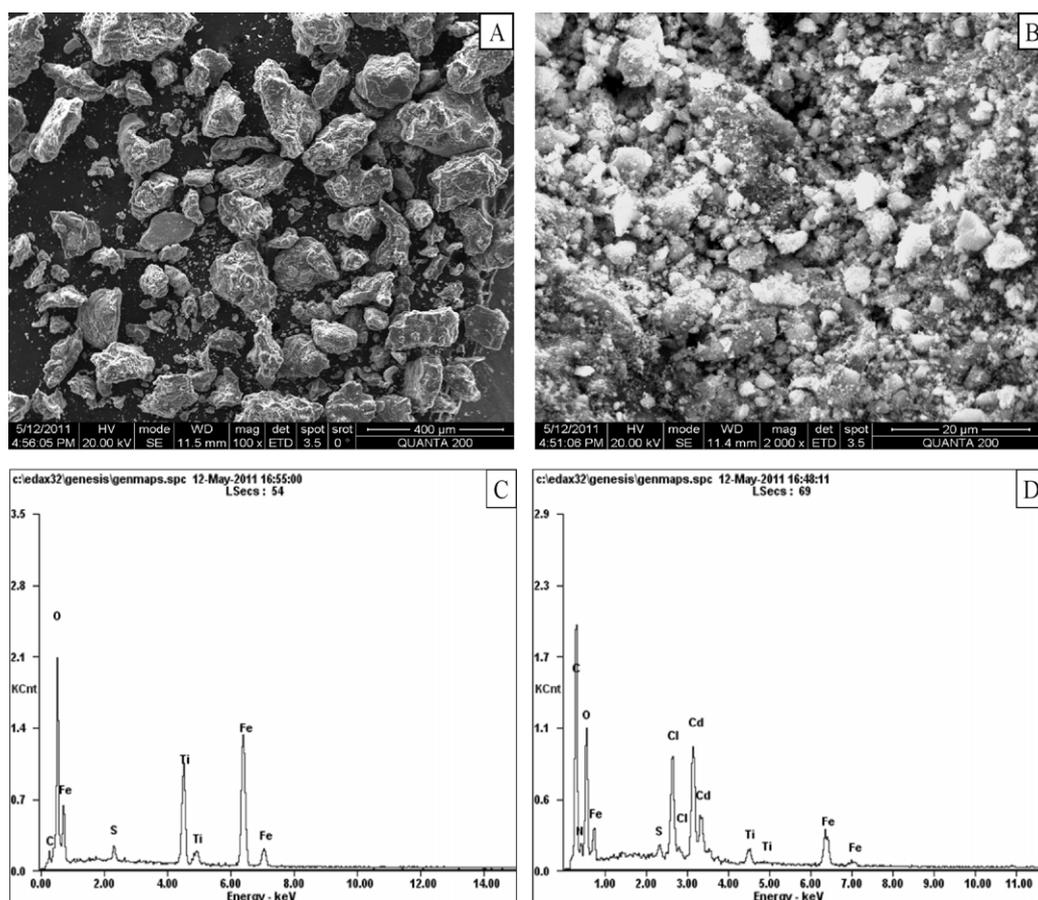
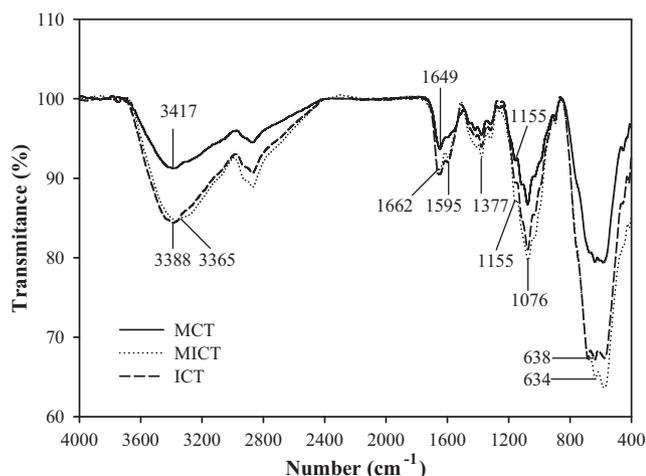
**Fig. 6.** SEM-EDX micrographs of MICT: (A) SEM image of MICT ($\times 100$), (B) SEM image of MICT ($\times 2000$), (C) EDX of MICT before adsorption, (D) EDX of MICT after adsorption.

Table 3
GC/MS spectral data of photodegraded products of 2,4-DCP.

Peak no.	Retention time (min)	M_w (m/z)	Assignment	Molecular formula	CAS no.
1	4.20	106.17	Dimethylbenzene	C_6H_{10}	95-47-6
2	4.28	118.17	Butoxyethanol	$C_6H_{14}O_2$	111-76-2
3	4.47	100.16	Cyclohexanol	$C_6H_{12}O$	108-93-0
4	4.72	126.59	3-Chlorotoluene	C_7H_7Cl	108-41-8
5	4.88	94.11	Phenol	C_6H_6O	108-95-2
6	5.03	108.09	1,4-Benzoquinone	$C_6H_4O_2$	106-51-4
7	5.35	-	Background	$Si(R)_4$	-
8	6.42	162	2,4-Dichlorophenol	$C_6H_4Cl_2O$	120-83-2
9	6.55	128.5	4-Chlorophenol	C_6H_5ClO	106-48-9

**Fig. 7.** FT-IR spectra of the prepared adsorbents.

including 4-chlorophenol, 1,4-benzoquinone, phenol, cyclohexanol, and some other trace substances (Fig. 8 and Table 3). Based on the intermediates identified, reductive dechlorination and reaction with hydroxyl radical were proposed as the major decomposition route.

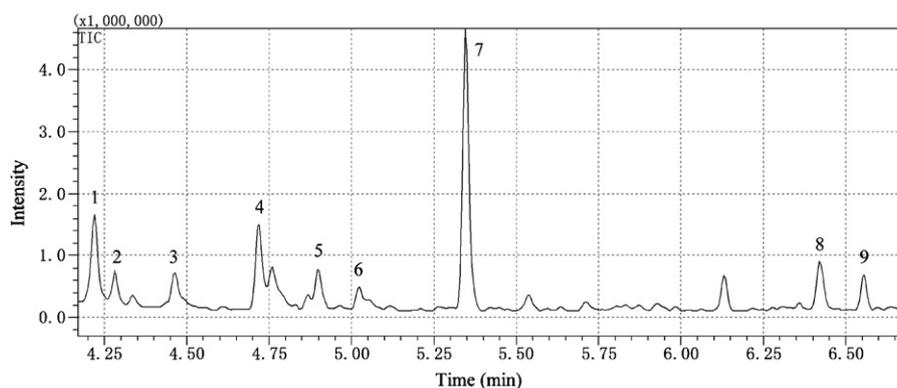
In our research, TiO_2 was used as catalyst and the mixture was shaken under UV light. The ability of semiconductor photocatalysts to remove pollutants is based on the active oxidising species they form as they are irradiated [53]. Hole is produced as a result of photoinduced charge separation which may then cause the formation of hydroxyl radical by direct hole transfer reaction with $\cdot OH$. Hydrogen peroxide may be generated via chain reactions involving conduction band electron. Even though hole and hydrogen peroxide may aid the degradation of chlorophenols, experimental evidences have proved the main oxidant to be hydroxyl radical [54,55]. Therefore, we propose the mechanistic pathways in Fig. 9 to account for the photoproducts of 2,4-DCP degradation encountered

in this study. The cleavage of substituent $-Cl$ group has been shown to be the first process in the photocatalytic destruction of chlorophenols [52]. Thus, 4-chlorophenol can be produced by the cleavage of ortho- Cl of 2,4-DCP ring. Reductive dechlorination of 4-chlorophenol can result in the formation of phenol. In addition, 2,4-DCP can react with photogenerated $\cdot OH$ radical to form 2-chlorohydroquinone and then to 1,4-benzoquinone.

The two identified special intermediate species, namely, dimethylbenzene and 3-chlorotoluene have not been reported elsewhere even in 2,4-DCP degradation by other advanced oxidation processes. These compounds have one or two higher carbon atoms with regard to 2,4-DCP and were formed during the photodegradation of chlorophenols. The formation processes of these two intermediates are proposed as follows: (i) 2,4-DCP homolysis at Cl -ring would form chlorine-hydroxyphenyl radical which could either yield 3-chlorotoluene via methylation; and (ii) the methylated form could undergo further reductive dechlorination, and then methylate again to form dimethylbenzene. The formation of higher carbon intermediates during the photodegradation of chlorophenols is not rare. The methylated intermediates have also been detected by Fukushima and Tatmisi [56] during the photodegradation process of pentachlorophenol which supports our identification. The formation of benzoic acid and 4-hydroxybenzaldehyde as intermediate products during the photocatalytic degradation of 2,4-DCP in different systems have also been reported [53,57]. The suggested tentative mechanistic key factor to the formation of such species is the presence of methyl radicals produced in situ during the photocatalytic degradation of chlorophenols. Therefore, an initial dechlorination of chlorophenol via a homolytic cleavage of aryl- Cl bonds or interaction with the trapped electron on the photocatalyst surface is necessary [57].

3.6. Desorption and reuse

The recovery of adsorbents for recycling has been one of the most important aspects of research regarding the treatment of water and wastewater [58]. For any environmental purpose of a

**Fig. 8.** The gas chromatograms of 2,4-DCP after the photodegradation in the presence of MICT.

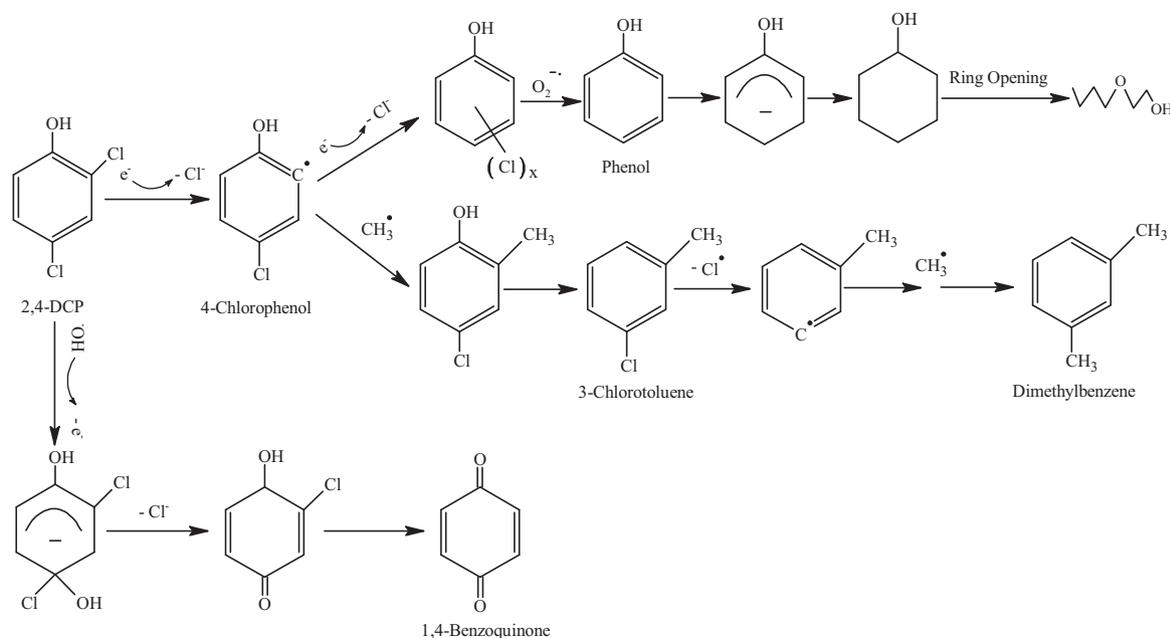


Fig. 9. Reaction scheme proposed based on the intermediates of 2,4-DCP photodegradation by MICT.

material, the repetitive usage provides clues for economic feasibility and resourcefulness. Due to a reversible absorption process, the regeneration of the adsorbent is possible [59]. Therefore, to investigate the reusability of the MICT, 0.1 mol/L EDTA was used as elution agent for the desorption of cadmium ions adsorbed onto the MICT composite sorbent. After the cadmium ions were desorbed, hydrogen ions of EDTA became available and adhered onto the surface of the sorbent. The important functional groups on the sorbent, such as $-\text{NH}_2$ and $-\text{COO}^-$, are protonated to $-\text{NH}_3^+$ and $-\text{COOH}$, leading to less metal binding on the sorbent [60]. Thus, 0.1 mol/L NaOH was applied to neutralize the hydrogen ions in the regeneration.

The amount of cadmium ions adsorbed and the desorption efficiency in five consecutive sorption-desorption cycles using EDTA are presented in Fig. 10. The desorption efficiency of each cycle is as high as 92.7% to 96.2%. The degradation capacities of the cycles were 84.1%, 80.8%, 78.3%, 73.9%, and 69.0%, respectively. Besides the high desorption ratio, the sorption and degradation capacities were barely affected by the number of cycles, implying the higher possibility of this adsorbent to recover cadmium and 2,4-DCP co-contaminated water.

4. Conclusion

A novel type of composite called MICT was developed for effective cadmium adsorption and 2,4-DCP degradation in the current study through the combination of ion-imprinted technology and photodegradation technology. The prepared adsorbent has better adsorption and degradation capacity compared with those previously reported. The maximum adsorption capacity of cadmium was 256.41 mg/g according to the Langmuir model and the 2,4-DCP degradation efficiency was up to 98% at the initial 2,4-DCP concentration of 10 mg/L. Several intermediates, such as 4-chlorophenol, 1,4-benzoquinone, phenol, cyclohexanol, and some other trace substances, were identified as intermediates based on GC/MS technology. Reductive dechlorination and reaction with hydroxyl radicals were proposed as the major decomposition route for 2,4-DCP in the presence of UV light. The adsorbed cadmium ion can be desorbed easily and the sorption and degradation capacities are barely affected by the number of cycles. The results obtained in the present study showed that the MICT composite is an ideal platform to accelerate the simultaneous disposal of heavy metals and organic pollutants in wastewater. The composite would be helpful in facilitating the development of processes that could be useful for the enhanced treatment of co-contaminants in the aquatic environment.

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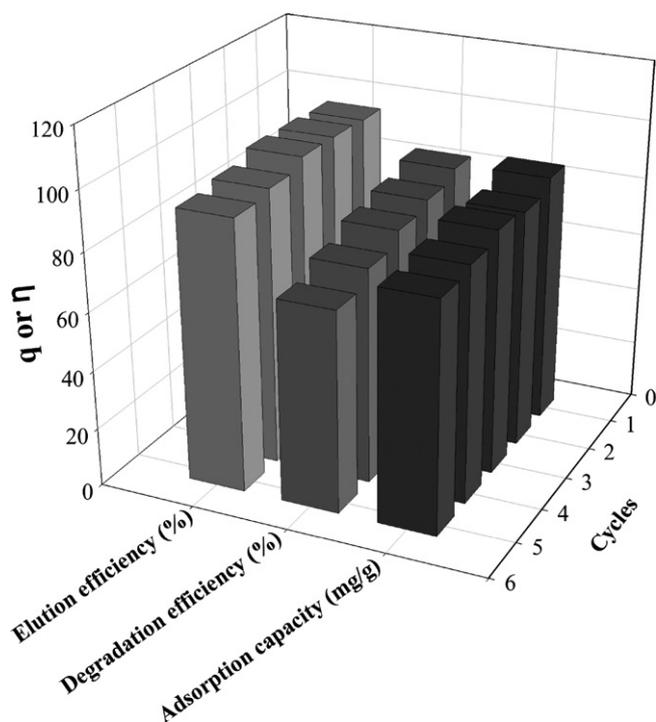


Fig. 10. The performances of MICT in different cycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2012.02.071.

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