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# Adsorption properties of Cd(II)-imprinted chitosan resin

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**Abstract** A Cd(II)-imprinted chitosan resin (Cd-ICR) was prepared for adsorption of Cd(II) from aqueous solutions. Batch adsorption experiments were performed to evaluate the adsorption conditions, selectivity and reusability as well as its application in the removal of Cd(II) from oyster hydrolysate. The results indicated that the maximum adsorption capacity of Cd-ICR was 0.795 mmol/g in sole Cd(II) solution at pH 5.0, 45 °C with equilibrium time 10 h. The selectivity coefficient of Cd(II) and other metal cations on Cd-ICR indicated an overall preference for Cd(II), which was much higher than that of non-imprinted chitosan resin. Cd-ICR could be reused for ten times with about 27% regeneration loss. FTIR spectra demonstrated that Cd(II) in Cd-ICR occurred on amino and secondary hydroxyl groups. The removal ratio of Cd(II) from oyster hydrolysate was 73.6%, while that of Ca(II) and Zn(II) were 6.2 and 9.9%, respectively. This suggests that Cd-ICR is a very promising adsorbent for selective removal of Cd(II) from aqueous solutions.

## Introduction

Cadmium(II) (Cd(II)) is attracting wide attention of environmentalists as one of the most toxic heavy metals. The major sources of Cd(II) release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1, 2]. Cd(II) is transferred into humans via food chain and drinking. The human body has no specialized physiological route for Cd(II) elimination. Cd(II) accumulates mainly in the kidneys and liver, but is also found in skeletal and muscular systems, and in the endocrine glands. Cd(II) adversely affects human health because of serious damage to kidney, renal disturbances and bones lesions. For example, an epidemic of Japanese itai–itai disease, which causes altered renal tubular function, impaired regulation of calcium and phosphorus, bone demineralization, osteomalacia and pathological fractures is believed to originate from the chronic ingestion of Cd(II) found in environment as a pollutant [3, 4]; hence, Cd(II) removal has become a challenging task for environmentalists.

The World Health Organization (WHO) has recommended the maximum permissible limit (0.005 mg/L) for Cd(II) in drinking water. Current treatments to remove Cd(II) from contaminated water are mostly based on chemical precipitation, electrocoagulation, membrane filtration, ion exchange and reverse osmosis [5–9]. However, these methods have many disadvantages such as ion exchange plants and membrane separation require high maintenance and operation costs, chemical precipitation is capable of removing trace levels of heavy metal ions, furthermore, its precipitates are difficult to be separated due to their settling characteristics. The numerous chitosan-based beads have already been explored as an adsorbent for the removal of Cd(II) ions from aqueous solutions [10, 11]. Thus, to develop natural, renewable, and low-cost adsorbent alternatives to synthetic polymer for the removal of heavy metal ions especially Cd(II) ions from wastewater are highly interested for human life.

Chitosan is the *N*-deacetylation product of chitin, a biopolymer that can be formulated into beads and films, the major component of the shells of crustacean organisms and the second most abundant naturally occurring biopolymer

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next to cellulose. Chitosan have biological and chemical properties such as non-toxicity, biocompatibility, high chemical reactivity, chelation and adsorption properties [12–14]. The presence of amine groups makes a chitosan unique among biopolymers, for example, its cationic behaviour in acidic solutions and its affinity for heavy metal ions [15, 16]. Nowadays, chitosan is an excellent adsorbent and widely used in the form of beads/resin to adsorb heavy metal ions from contaminated water [17–19]. However, the selectivity of chitosan resin for specified metal ions was very low; it might adsorb a number of essential mineral elements besides heavy metal ions simultaneously, which restricted its application in the removal of named heavy metal (Cd(II)) from liquid food, such as beverage, hydrolysate and so on.

Molecular imprinting is an emerging technology that has gained much attention in generating recognition sites by reversible immobilization of template molecules on cross-linked macromolecular polymer matrixes. Due to the interaction between monomers and templates, the imprinted materials possess predetermined arrangement of ligands and tailored binding pockets, which behave affinity and selectivity for the template molecule over other structurally related compounds [20]. So far, many metal ions-imprinted polymers have been prepared, including Dy(III) [21], Gd(III) [22], $UO_2$(II) [23], Pd(II) [24], Cu(II) [25], Zn(II) [26, 27], Al(III) [28], Ni(II) [29], Ca(II) [30] and Mg(II) [31] imprinted ones. Some interest has been focused on the preparation of various novel Cd(II)-imprinted polymers. Gawin et al. [32] prepared Cd(II)-imprinted beads and used as a minicolumn packing for flow-injection-flame atomic absorption spectrometry determination of cadmium(II) in water samples. Singh and Mishra [33] synthesized a new imprinted polymer for selective solid phase extraction (SPE) of Cd(II) from aqueous solutions. Segatelli and Santos [34] reported $Cd^{2+}$-imprinted poly(ethylene glycol dimethacrylateco-vinylimidazole) for selective extraction/preconcentration of $Cd^{2+}$ ions from aqueous solution. But these synthesized imprinted polymers are not be aimed at liquid food and not applied in the selective removal of Cd(II) from oyster hydrolysate.

Oyster hydrolysate is the hydrolysis product of Pacific oyster (*Crassostrea gigas*), which is one of filter-feeding bivalves. It is known that oyster could accumulate Cd(II) easily [35, 36] and the concentration of Cd(II) might reach up to 129 mg/kg (dry weight) [37] when growing in contaminated regions; however, oyster hydrolysate contains all of the trace elements needed by the body, especially zinc [38]. By now, there is no suitable materials or methods reported in the literature to remove Cd(II) from the hydrolysate.

The aim of this study is to prepare Cd(II)-imprinted chitosan resin to evaluate the adsorption property for Cd(II) ions as well as its application in the selective removal of Cd(II) from oyster hydrolysate. The adsorption mechanisms of Cd-ICR and NICR for Cd(II) have also been characterized by means of FTIR spectra.

## Experimental

### Materials

Chitosan (CTS) (degree of deacetylation = 95.4%, $M_w = 5.0 \times 10^5$ Da) was purchased from Haihui Bioengineering Co., Ltd (Qingdao, China). Metal ions standards were all obtained from National Steel Material Test Center (Beijing, China). Acetic acid, cadmium chloride, liquid paraffin, ethyl acetate, glutaraldehyde and all the other reagents used in this experiment were of analytical grade or better and used as received without further purification. Deionized distilled water (DDW) (Millipore, Spain) was used throughout the experiments.

### Preparation of Cd(II)-imprinted chitosan resin

The experimental procedure for the preparation of Cd(II)-imprinted chitosan resin was described as follows. Firstly, a total of 30.0 g chitosan was added to 600 mL 0.02-M $CdCl_2$ aqueous solution, shaking for 24 h at 30 °C. The mixture was filtered under reduced pressure, and then washed with DDW until Cd(II) could not be detected in the filtrate. The residue was dried in a vacuum oven at 50 °C.

Afterward, amount of 10.0 g of the above product was swelled in 200 mL 2% acetic acid solution. As for the preparation of a dispersion phase, liquid paraffin and ethyl acetate was heated up to 40 °C, stirring for 20 min at 300 rpm. After that, the system was heated up to 60 °C, stirring for 3 h at 175 rpm, meanwhile, glutaraldehyde was added as a crosslinking agent to generate polymeric beads. The final beads were extensively washed with petroleum ether, acetone, ethanol and DDW in sequence to remove any unreacted fraction [39]. And then, the template molecule (i.e., $Cd^{2+}$) was removed from the polymer beads using 0.1-M HCl. The wet resin was collected and dried in a vacuum oven at 50 °C, abbreviated as Cd-ICR. As a control, non-imprinted chitosan resin (NICR) was prepared under identical experimental conditions without adding Cd(II).

### Adsorption experiments

#### *Single metal ion adsorption*

Batchwise experiments were conducted in 50-mL Erlenmeyer flasks. Accurately, 0.2 g of Cd-ICR and NICR were added to 25 mL of single metal ions solution (initial concentration 0.02 M), respectively, shaking for 24 h at 25 °C, and then filtered. Cd(II) concentration of the filtrate was measured with a flaming atomic absorption spectrophotometer (FAAS) (AA-6800, Shimadzu Ins) at 228.8 nm wavenumbers.

The amount of Cd(II) ions adsorbed per unit mass of the Cd-ICR was calculated using the following equation:

$$q_e = \left(\frac{C_i - C_e}{W}\right)V \tag{1}$$

where $q_e$ is the adsorption capacity of the beads (mg/g), $C_i$ and $C_e$ are the concentrations of Cd(II) in the initial and equilibrium solution (mg/L), respectively, $V$ is the volume of the aqueous solution (L) and $W$ is the mass of dry beads (g).

### *Mixed metal ions adsorption*

Amount of 0.2 g of Cd-ICR or NICR were added to 25 mL of mixed metal chloride solution containing Cd(II), Ca(II) and Zn(II) (initial concentration of single species 0.02 M), shaking for 24 h at 25 °C, and then filtered. The adsorption capacities of Cd-ICR and NICR for M(II) were calculated using Eq. 1.

## Reusability experiment

Several solvents/solutions (HCl, $HNO_3$, NaCl, EDTA) were tried to regenerate the biosorbents. Out of the solvents/solutions, 0.1-M HCl aqueous solution was found to be effective in desorbing Cd(II) ions from the loaded adsorbents. The Cd-ICR was regenerated in 0.1 M HCl aqueous solution and stirred at room temperature, the procedure was repeated for many times until Cd(II) could not be detected in the filtrate. Then, Cd-ICR was washed thoroughly with DDW to a neutral pH. The regenerated Cd-ICR was reused in the following adsorption experiments and the procedure was repeated for 10 times by using the same Cd-ICR.

## Characterization

Fourier Transform Infrared Spectra (FT-IR, Nexus 470, Nicolet, USA) of Cd-ICR and NICR before and after Cd(II) adsorption were obtained and all samples were prepared as a potassium bromide tablet (1 mg of the powder was blended with 100 mg of IR-grade KBr in an agate mortar and pressed into a tablet).

## Application of Cd-ICR in the removal Cd (II) from oyster hydrolysate

One gram of Cd-ICR and NICR were added to 10 mL of oyster hydrolysate, respectively, shaking for 24 h at 40 °C, and then filtered. One milliliter of the separated hydrolysate was digested after mixed with 5-mL $HClO_4$ at 180 °C. The concentration of metal ions was measured by FAAS.

# Results and discussion

## Optimum Cd(II) adsorption conditions of Cd-ICR and NICR

### *Effect of temperature on Cd(II) adsorption*

The adsorption capacity of Cd-ICR for Cd(II) increased as the temperature is raised from 25 to 45 °C (Fig. 1). Because the adsorption was an endothermic process, the higher temperature is to the advantage of the adsorption. It is apparent that at the lower temperature (<45 °C), the adsorption of Cd(II) on Cd-ICR or the formation of Cd-ICR with Cd(II) complexes is unfavoured. However, when the temperature exceeded 45 °C, a higher temperature favored desorption or dechelation, thus 45 °C was chosen as the optimum temperature for the adsorption of Cd(II) onto Cd-ICR [40].

### *Effect of pH on Cd(II) adsorption*

The comparison of adsorption performance would require an optimum pH for adsorption of different metals before a well-founded conclusion could be reached. The chelating process of metal ions was sensitive to pH and usually adsorption did not occur at low pH [41]. Hence, the effect of pH on the chelation between Cd-ICR and Cd(II) was also investigated. The precipitation of Cd(II) as hydroxide

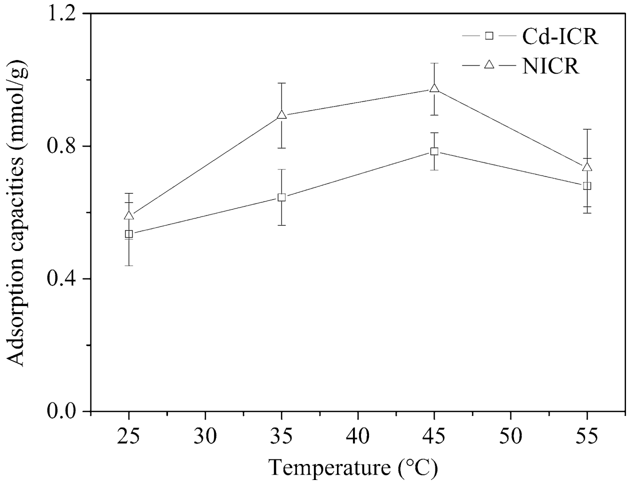

**Fig. 1** Relationship between temperature and adsorption capacities of Cd-ICR and NICR for Cd(II) (adsorption conditions: initial Cd(II) concentration 0.02 M, shaking for 24 h)

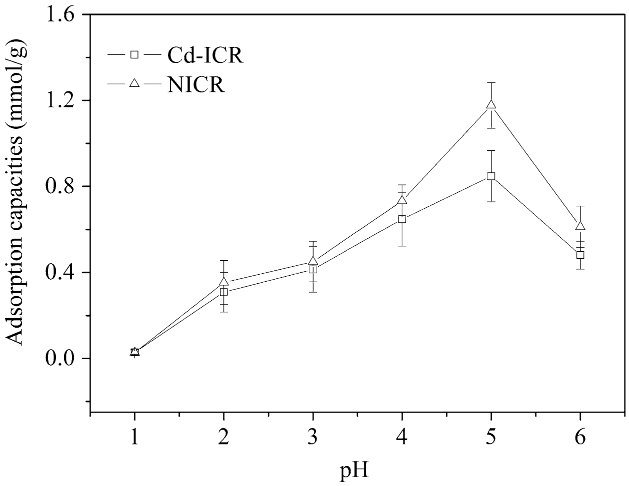

**Fig. 2** Relationship between pH and adsorption capacities of Cd-ICR and NICR for Cd(II) (adsorption conditions: initial Cd(II) concentration 0.02 M, shaking for 24 h at 45 °C)

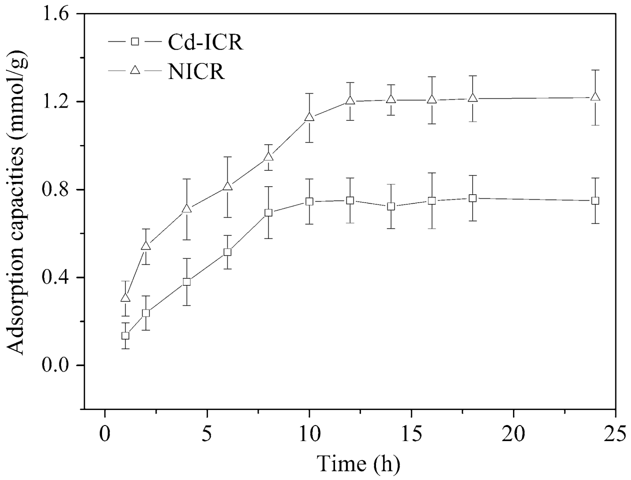

**Fig. 3** Relationship between contact time and adsorption capacities of Cd-ICR and NICR for Cd(II) (adsorption conditions: initial Cd(II) concentration 0.02 M, shaking for 24 h at 45 °C)

was found to occur in basic solution [42]; therefore, all adsorption experiments were carried out in low acidic medium at pH < 7.0.

The adsorption capacities of Cd-ICR and NICR increased when pH changed from 1.0 to 5.0 and attained the maximum value of 0.77 and 1.18 mmol/g at pH 5.0 (Fig. 2). A further increase or decrease of pH decreased the adsorption capacity of Cd-ICR. This common feature is explained by a general ion exchange equilibrium involving the Cd-ICR, Cd(II) and $H^+$ [43]. In acidic medium (pH < 7) due to high $H^+$ concentration, active sites of the adsorbent were protonated and leads to the prevention of metal ions adsorption [44]. However, with the increasing of pH, deprotonation of chitosan amino groups take place and hence the adsorption of Cd(II) increased [45].

### *Effect of contact time on Cd(II) adsorption*

The effect of contact time on the adsorption of Cd(II) is shown in Fig. 3. Initially, the adsorption rate was faster up to 8 h and the maximum adsorption of Cd(II) occurred. The equilibrium time was observed around 10 h, and beyond this time no change in adsorption was occurred. Thus, the equilibrium time was maintained 10 h in the subsequent adsorption studies. In the beginning of fast adsorption, it may be explained due to the availability of more number of adsorption sites [46]. After the initial adsorption, the available sites in the adsorbent reduced and thus rate of adsorption further decreased [47], which attained a limiting value at equilibrium. Rate of adsorption is of great significance for developing the adsorbent-based water technology [48]. Thus, the ability of developed beads to adsorb the maximum amount of Cd(II) within 10 h indicates its suitability as an effective adsorbent. Hence, it was reasonable that the adsorption time set on 24 h in the forenamed experiment assuring adequate time to reach adsorption equilibrium had no effect on adsorption capacity.

## Selective adsorption of Cd-ICR for metal ions

### *Adsorption for single metal ion*

Table 1 shows the adsorption capacities of Cd-ICR and NICR for four metal ions. The adsorption capacities of Cd-ICR and NICR for the metal ions were in the following order: Cd(II) > Zn(II) > Cu(II) > Ca(II) and Cu(II) > Cd(II) > Zn(II) > Ca(II), respectively. The adsorption capacity of Cd-ICR for Cd(II) was highest among the mixed metal ions, while the adsorption capacity of NICR for Cd(II) was lower than Cu(II). This was attributed to the formation of new inter-chain linkages, resulting in some restriction in the polymer network and the loss of the chain flexibility as well as the presence of three-dimensional network structure, which was better fit for chelating Cd(II) rather than other metal ions. It is shown in Table 1, the adsorption capacity of Cd-ICR for Cd(II) was followed by Zn(II), because Cd(II) and Zn(II) were of the group IIB, they have many similar chemical properties. Therefore, the adsorption selectivity of Cd-ICR for Cd(II) was higher than that of NICR. This was consistent with the adsorption of Cd-ICR from mixed metal ions, Cd(II) was adsorbed onto Cd-ICR prior to other two metal ions (Fig. 4). Sun prepared cross-linked carboxymethyl-chitosan resin with Zn(II) as template ion, the selective adsorption for Zn(II) was higher than non-imprinted carboxymethyl-chitosan resin [49], which further suggested that Cd-ICR could adsorb Cd(II) prior to other metal ions.

**Table 1** Adsorption capacities (mmol/g) of Cd-ICR and NICR for single metal ion

| Adsorbents | Cd(II) | Cu(II) | Ca(II) | Zn(II) |
|---|---|---|---|---|
| Cd-ICR | 0.795 ± 0.091 | 0.519 ± 0.071 | 0.235 ± 0.130 | 0.731 ± 0.133 |
| NICR | 1.202 ± 0.145 | 1.256 ± 0.082 | 0.439 ± 0.126 | 0.988 ± 0.064 |

Adsorption conditions: 0.20 g of Cd-ICR and NICR, shaking for 24 h at 45 °C, the initial concentration of single metal ions is 0.02 M

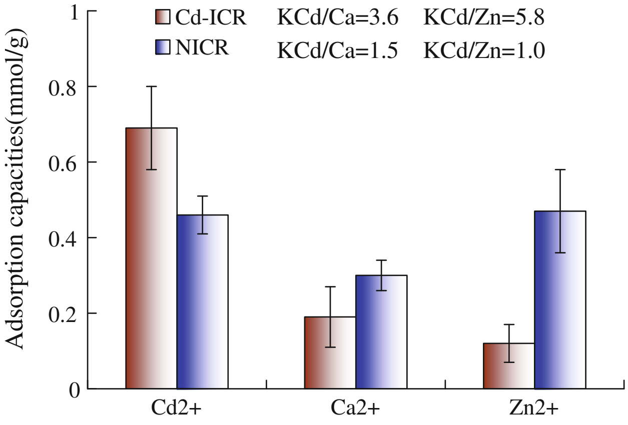

**Fig. 4** Selective adsorption of Cd-ICR and NICR in the coexistence of Cd(II)–Ca(II)–Zn(II) chloride solution (adsorption conditions: initial concentration of M(II) 0.02 M, shaking for 24 h at 45 °C)

### *Co-adsorption for three mixed metal ions*

To further investigate the selective adsorption of Cd-ICR when compared with NICR, the adsorption capacities of the two resins for Cd(II), Ca(II) and Zn(II) from mixed chloride solution at pH 5.0 was compared. As shown in Fig. 4, the selective adsorption of Cd-ICR for Cd(II) was higher than that of NICR. In the adsorption of mixture chloride solution, the selectivity coefficient ($K_{Cd^{2+}/Ca^{2+}}$ and $K_{Cd^{2+}/Zn^{2+}}$) of Cd-ICR was higher than that of NICR. This result suggested that Cd-ICR have higher selectivity for template metal ions in the mixed metal ions than that of NICR. That was because of the formation of Cd-ICR leads to some restriction of new inter-chain linkages in the polymer network structure and the loss of the chain flexibility, resulting in a decrease of accessibility and a descent of adsorption capacities for other metal ions [50, 51]. Hence, it could be concluded that Cd-ICR would be an effective adsorbent to selectively adsorb Cd(II) from mixed metal ions solution.

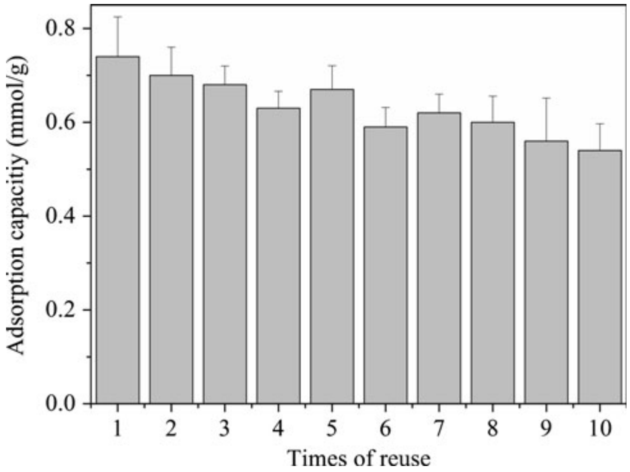

**Fig. 5** Relationship between the times of reuse and adsorption capacity of Cd-ICR for Cd(II) (adsorption conditions: initial Cd(II) concentration 0.02 M, shaking for 24 h at 45 °C, the concentration of regeneration solution 0.10 M HCl)

### Reusability

Desorption studies help to reveal the nature of adsorption process and to recover the Cd(II) ions from Cd-ICR. As can be seen from Fig. 5, it was revealed that the adsorption capacity of Cd-ICR for Cd(II) decreased slightly from 0.74 to 0.54 mmol/g with increasing the times of reuse because some adsorption sites was destroyed by HCl in the desorption process. However, Cd-ICR could be reused for ten times with about 27% regeneration loss, which indicated that Cd-ICR had a good reusability.

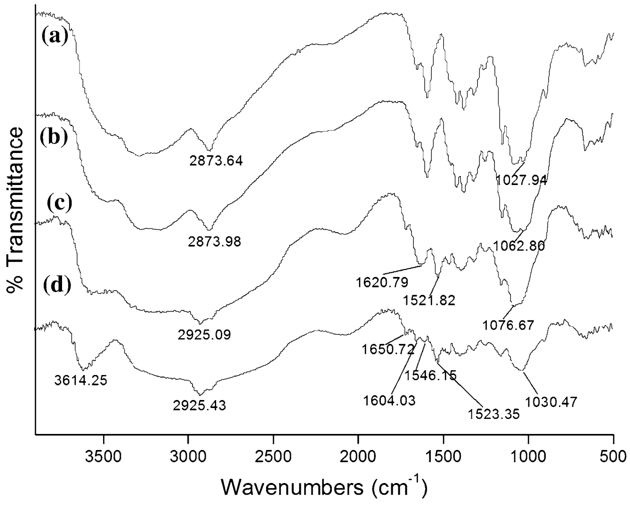

**Fig. 6** FT-IR spectra of NICR before (*a*) and after (*b*) and Cd-ICR before (*c*) and after (*d*) Cd(II) chloride adsorption (adsorption conditions: initial Cd(II) concentration 0.02 M, shaking for 24 h at 45 °C)

**Table 2** The concentration of different metal elements before and after removed by Cd-ICR and NICR from Pacific oyster hydrolysate

| Element | Stock solution (mg/L) | Solution treated by Cd-ICR (mg/L) | Solution treated by NICR (mg/L) |
|---|---|---|---|
| Cd | 0.1956 ± 0.0228 | 0.0517 ± 0.0050 | 0.0756 ± 0.0038 |
| Cu | 0.1099 ± 0.0113 | 0.0881 ± 0.0028 | – |
| Ca | 9.2816 ± 0.8213 | 8.7075 ± 0.4780 | 7.8271 ± 0.3657 |
| Zn | 3.0302 ± 0.3123 | 2.7295 ± 0.2675 | 1.2235 ± 0.3103 |

*Note*: removal conditions: resin/hydrolysate 1:10 (m/v), contact temperature 40 °C

– no detect

### FTIR spectra of Cd-ICR

The FTIR spectra of NICR before (a) and after (b) adsorbed Cd(II), Cd-ICR before (c) and after (d) adsorbed Cd(II) were shown in Fig. 6. According to 6a and b, the absorb bands at 1028 $cm^{-1}$, associated with the stretching of C–N bond, weakened and shifted to higher wave numbers, which indicated the formation of N–Cd bond in the adsorption process and the vibration of C–N affected by steric effect, resulting in a shift to higher wave numbers (1062 $cm^{-1}$), which revealed that Cd(II) was adsorbed via $–NH_2$ group, forming the steric structure of N–Cd.

The absorb bands at 1077 $cm^{-1}$, associated with the stretching of the secondary –C–OH, have a significantly downward shift (Fig. 6c, d) and the intensity become stronger. The absorb bands at 1152 $cm^{-1}$, corresponding to the stretching of C–N bond weaken and shifted to higher wave numbers, which indicated the formation of N–Cd bond in the adsorption process. These results revealed that the N and O atoms in the Cd-ICR participated in coordination with Cd(II). Thus, the reaction was a chelation process, forming the –N–Cd–O– steric structure.

The absorb bands observed at 502 and 449 $cm^{-1}$, assigned to stretching vibration of N–Cd and O–Cd, reconfirmed that the amino group and the hydroxide group participated in the coordination [52].

From the above FTIR analysis, it can be concluded that the amino group ($–NH_2$) and the secondary hydroxyl group (–OH) participated in the Cd-ICR chelation process.

### Application of Cd-ICR

Cd-ICR had good removal of Cd(II) from oyster hydrolysate. It was showed that 73.6% of Cd(II) was removed at the ratio of 1:10 (Cd-ICR/hydrolysate, m/v) at 40 °C, compared with 62.9% of Cd(II) was removed by NICR at initial conditions (Table 2). However, other metal elements such as Ca(II) and Zn(II) were removed less than that of NICR. Hence, Cd-ICR had promising application in the selective removal of Cd(II) from oyster hydrolysate. The removal rate of Cd(II), Ca(II) and Zn(II) from the hydrolysate was 73.6, 6.2 and 9.9%, respectively. It was concluded that Cd-ICR is an effective sorbent to selectively adsorb Cd(II) from aqueous solution and the problem of superfluous Cd(II) in the hydrolysate is to be solved.

## Conclusions

In summary, it was found that the maximum adsorption capacity of Cd-ICR for Cd(II) was 0.795 mmol/g at pH 5.0, 45 °C and equilibrium time 10 h. Furthermore, the selectivity of Cd-ICR for Cd(II) was greatly enhanced when compared with NICR. It was also revealed that Cd-ICR could be reused for ten times with about 27% regeneration loss. The FTIR spectra revealed that the adsorption of Cd-ICR for Cd(II) was a chelation process through both nitrogen and oxygen of secondary hydroxyl group coordinated with Cd(II) in the polymer chains, while the adsorption of NICR for Cd(II) was a physical adsorption process. The Cd-ICR had promising application in the removal of Cd(II) from oyster hydrolysate, the removal rate was 73.6% when compared with 6.2, 9.9% of Ca(II) and Zn(II), respectively. Therefore, Cd(II) was selectively removed by Cd-ICR. It is the author's hope that this result will be helpful for researchers who are interested in synthesizing and applying chitosan resins to remove Cd(II) from aqueous solution and oyster hydrolysate as well as its derivatives in the future.

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