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Preparation of Porous Chitosan Microsphere Absorbent and Research on Its Absorption Ability for Cu^{2+} and Zn^{2+}

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Abstract

An amino chitosan absorbent has been prepared with monoethylamine, chitosan, catalyst, cross-linking agent, hydroxylpropyl chlorination agent and amination agent. This paper discusses the effect of monoethylamine modification on the amino content in chitosan absorbent, as well as its effect on the absorption capacity of absorbent for Cu^{2+} and Zn^{2+}; and investigates the absorption kinetics of chitosan and amino chitosan for Cu^{2+} and Zn^{2+}. The results indicate that the amino content of modified porous microspheric chitosan is higher than that of chitosan; its absorption capacity for Cu^{2+} and Zn^{2+} increases with the rise of temperature and changes with pH, and there is no obvious difference in absorption capacity of Zn^{2+} between chitosan and modified chitosan.

Keywords: Chitosan, Absorbent, Amination

The major use of chitosan is to purify wastewaters. At present, people are growing concerned that heavy metals, insecticides and their accumulations in food chains will cause ecological damages and health hazard. Therefore, wastewater is required to be treated before discharge. Amino group in chitosan can form a coordinate-covalent bond with metal ion. As a result, chitosan has been widely applied in wastewater treatment. Chitosan exhibits excellent properties in collecting heavy metal ions (Jeon C *et al*, 2005, p. 3938-3944; Rojas G *et al*, 2005, p. 31-36). Amino group and hydroxyl group in chitosan molecular can react with metal ions, such as Hg^{2+}, Cu^{2+} and Zn^{2+}, to form stable chelates (Guibal E *et al*, 2002, p. 149-163; Ruiz M *et al*, 2000, p. 155-173; Guibal E *et al*, 1999, p. 4011-4022), and effectively remove toxic heavy metal ions from industrial wastewaters (Guibal E *et al*, 1999, p. 4011-4022). Therefore, application of chitosan has been of great significance in environmental protection.

There has been a great deal of research in this field home and abroad. Although starting relatively late in China, it has developed rather rapidly, and got many achievements. Amino group and hydroxyl group in chitosan molecular exhibit good activity against metal ions, and can introduce functional groups onto chitosan by acylation, etherification, N-alkylation, esterification or other reactions. The obtained derivatives have better physical and chemical properties, higher solubility, and stronger chelating ability towards heavy metal ions. This study has increased the amino content of chitosan and improved its absorption ability for Cu^{2+} and Zn^{2+} by modification of chitosan with ethylamine.

1. Experiment

1.1 Reagents and equipments

(1) Reagents

Chitosan with a deacetylation degree of 90.3%, from Shanghai Kabo Industrial and Trading Company; monoethylamine, from Shanghai Linger Chemical Co., Ltd.; copper nitrate trihydrate, from Taiyuan Xinli Chemical Co., Ltd.; zinc nitrate hexahydrate, from Shanghai Shicheng Chemical Co., Ltd.; oxalic aldehyde with mass fraction of 40%, from Guangzhou Wanyou Chemical Co., Ltd.; epichlorohydrin (AR), from Shanghai Reagent Company; sodium lauryl sulfate, from Shanghai Chemsun Trade Co., Ltd.; isopropanol (AR), acetone (AR) and acetic acid (AR), from Tianjin Damao Chemical Reagent Factory; ethyl acetate, from Yixing Huihuang Chemical Reagent Factory; ethanol, from Guangdong Zhongneng Alcohol Co., Ltd.; and self-made distilled water.

(2) Equipments

Nicolet-410 infrared spectrometer, PE 300 atomic absorption spectrophotometer, SHA-B water bath constant temperature oscillator, DZF-6050 vacuum dryer, all-glass syringe, and freeze dryer.

1.2 Preparation method

1.2.1 Preparation of metal ion solution

Accurately weigh and dissolve 23.7734 g of $Cu(NO_3)_2 \cdot 3H_2O$, then dilute to the mark in a 250 mL volumetric flask to obtain a Cu^{2+} standard solution with concentration of 6.2523 g/L (0.09840 mol/L), which is in turn diluted 10 times for further use.

Accurately weigh and dissolve 29.2710 g of $Zn(NO_3)_2 \cdot 6H_2O$, then dilute to the mark in a 250 mL volumetric flask to obtain a Zn^{2+} standard solution with concentration of 6.4324 g/L (0.09840 mol/L), which is in turn diluted 10 times for further use.

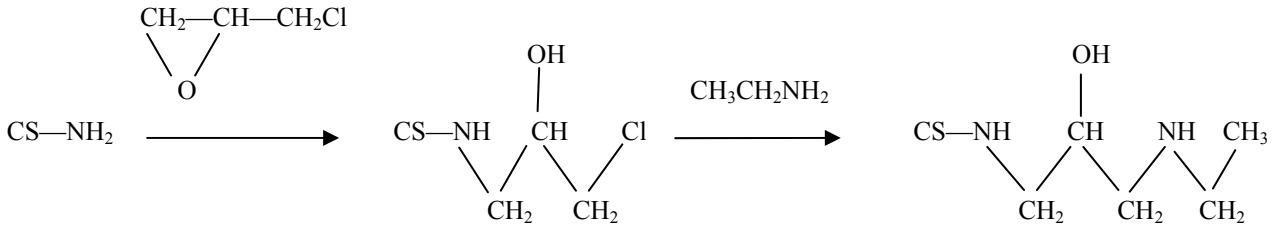
1.2.2 Preparation of porous chitosan microsphere (CS)

Weigh 3 g chitosan with deacetylation degree of 90.3% into flask, and dissolve with 100 mL 11% solution of acetic acid. Add 1.5 mL sodium dodecyl sulfate (emulsifier) into the above-formulated solution to obtain a 3% chitosan colloid solution, which is in turn placed at room temperature overnight to dissolve completely. Extract a certain amount of chitosan colloid solution with a syringe, and drop at a constant speed into a coagulant, which is prepared by adding 15 mL acetic acetate into 250 mL 2.8% solution of NaOH. The obtained sample is placed at room temperature for 2 h, and washed repeatedly with deionized water to get neutral chitosan microsphere, which is freeze dried for further use.

Add 2.5 mL oxaldehyde crosslinking agent into the above-mentioned chitosan microsphere, and stir intermittently for 3 h to get porous chitosan microsphere, which is in turn washed repeatedly with water and ethanol to remove the unreacted crosslinking agent, and air dried for further use.

1.2.3 Preparation of monoethylamine modified chitosan microsphere (ECS)

Introduce the prepared CS into 60 mL isopropanol in a 250 mL flask to obtain a suspension with the chitosan microsphere floating on the top surface. Add a mixture of 5 mL epichlorohydrin and 100 mL water solution of acetone (the volume ratio of acetone to water is 1:1) into the suspension, which is in turn stirred at 60 ℃ for 30 h, and let stand for separation. The solid phase is transferred into 150 mL water solution of ethanol (the volume ratio of water to ethanol is 1:1), followed by mixing with 6 mL monoethylamine. The obtained mixture is stirred at 50 ℃ for 10 h, then filtrated, washed and vacuum dried to get ECS. The reaction procedure is expressed with following formula.



1.3 Analysis methods

1.3.1 IR analysis

The sample is dried, crushed and pressed with KBr for IR spectrum measurement and interpretation.

1.3.2 Determination of amino content in ECS

Determine the amino content in ECS by volumetric method. Introduce 0.1 g ECS into 20 mL 0.5 mol/L solution of HCl, keep stationary for 48 h until the reaction reaches equilibrium, then titrate with 0.05 mol/L solution of NaOH. Calculate the molality of amino (b, mmol/g) with following formula.

$$b=20(C_0-C_1)/0.1$$

Here, C_0 (mol/L) and C_1 (mol/L) represent the initial concentration and equilibrium concentration, respectively.

1.3.3 Determination of absorption of metal ions

(1) Determination of absorption of Cu^{2+}

Determine the absorption of Cu^{2+} with PE 300 atomic absorption spectrophotometer under the conditions of 3.0 L/min ethyne flow rate, 10.0 L/min air flow rate, 0.7 mm slit width, 324 nm wavelength, and distilled water as blank.

(2) Determination of absorption of Zn^{2+}

Determine the absorption of Zn^{2+} with PE 300 atomic absorption spectrophotometer under the conditions of 3.0 L/min ethyne flow rate, 10.0 L/min air flow rate, 0.7 mm slit width, 213.0 nm wavelength, and distilled water as blank.

2. Results and discussions

2.1 IR spectrum measurements and interpretations of different chitosans

Figure 1~3 exhibit the IR spectrums of oxaldehyde-crosslinked chitosan, epichlorohydrin-modified chitosan and monoethylamine-modified chitosan, respectively.

Figure 1 exhibits a characteristic peak of Schiff's base at 1660~1680 cm^{-1}, which indicates that chitosan has crosslinked with oxaldehyde to obtain a Schiff's base. Figure 2 exhibits a characteristic peak of C=N at 1660~1680 cm^{-1} and a characteristic peak of C–Cl at 690~670 cm^{-1}, however no characteristic peak of C–O–C at 1280~1230 cm^{-1}, which indicates that chitosan has reacted with epichlorohydrin. The characteristic peak of C–Cl at 690~670 cm^{-1} has disappeared in figure 3, which demonstrates that Cl has been substituted by N in monoethylamine to obtain an absorbent of high amino content.

2.2 Determination of amino content in ECS

Table 1 shows the amino contents in chitosan and its derivatives.

2.3 Absorption of metal ions

2.3.1 Absorption dynamics of chitosan and modified chitosan for Zn^{2+} and Cu^{2+}

Weigh two samples of 0.5 g amino chitosan each in conical flasks, introduce the self-made solutions of Cu^{2+} and Zn^{2+}, respectively, and seal them well, which are in turn placed in an oscillator of constant temperature, and vibrated for absorption under the conditions of 25 ℃ and vibrating rate of 100 r/min. Determine the concentrations of Cu^{2+} and Zn^{2+} with an atomic absorption spectrophotometer per hour. Calculate the absorption capacity of chitosan for Cu^{2+} and Zn^{2+} with following formula.

$$Q = (C_0\text{-}C_e) \times V/m$$

Here, Q (mg/g) represents the absorption capacity; C_0 (mg/mL) represents the initial concentration of metal ion in solution; C_e (mg/mL) represents the equilibrium concentration of metal ion in solution; V (mL) represents the volume of solution; and m (g) represents the dosage of chitosan.

From figure 4 to figure 7, we can see that the absorption of modified chitosan for Cu^{2+} and Zn^{2+} reaches equilibrium after 8~9 hours of reaction; and the absorption of chitosan for Zn^{2+} changes little after modification, however, that for Cu^{2+} changes obviously. It's probably because that $–NH_2$ and adjacent –OH in chitosan chelate with Cu^{2+} to form a stable five-member ring, and linear-chain chitosan turns into a crosslinked polymer, this polymer will consist of more $–NH_2$ after modification, which further increases the absorption capacity for Cu^{2+}; However, the absorption for Zn^{2+} is realized mainly through –OH, and –OH content changes little after modification, therefore, the absorption of chitosan for Zn^{2+} changes little after modification.

2.3.2 Effect of temperature on absorption of modified chitosan for Zn^{2+} and Cu^{2+}

Dilute 25 mL standard solutions of Zn^{2+} and Cu^{2+} to the marks with distilled water in 250 mL volumetric flasks, respectively. Accurately weigh two samples of 0.15 g modified chitosan each in 250 mL conical flasks, and introduce 150 mL above-diluted solutions to obtain chitosan solutions with concentration of 0.1%. Seal them well, then place them into water bath of constant temperature of 5 ℃, 10 ℃, 15 ℃, 20 ℃ and 25 ℃, respectively. Stir at 80 r/min for 24 h, and measure the concentrations of Zn^{2+} and Cu^{2+} with atomic absorption spectrophotometer.

From figure 8, we can see that the absorption capacity of modified chitosan for Zn^{2+} or Cu^{2+} increases with the rise of temperature. The absorption capacity of modified absorbent for Zn^{2+} increases 41.5% from 97 mg/g to 139 mg/g, and that for Cu^{2+} increases 43.2% from 157 mg/g to 226 mg/g. It's probably because at high temperature, the absorbent molecular and absorbed ions move much faster, the interactions among molecular decrease, and the metal ions can move into absorbent more easier. As a result, the contact area between absorbent and metal ions increases, which leads to the increase of the absorption capacity of absorbent for metal ions. On the other hand, the absorption here is an endothermic procedure, therefore, the rise of temperature promotes the absorption of absorbent for metal ions.

2.3.3 Effect of pH on absorption of modified chitosan for Zn^{2+} and Cu^{2+}

Dilute 10 mL standard solutions of Zn^{2+} and Cu^{2+} to 100 mL with distilled water in 150 mL flasks, respectively, and prepare five samples for each group. Add 1 g modified chitosan into each sample, and place them in an oscillator with constant temperature of 20 ℃, vibrate for 24 h. Measure the concentrations of Zn^{2+} and Cu^{2+} with atomic absorption spectrophotometer, and calculate their absorption capacity.

From figure 9, we can see that the absorption capacity increases with the rise of pH at the beginning, and reaches the maximum when pH is 6~7, then decreases with the further increase of pH. It indicates that pH has an obvious effect on the absorption capacity. It's probably because the concentration of H^+ is high when pH is less than 6, and H^+ reacts with $–NH_2$ to form $–NH_3^+$, which causes the decline of effective concentration of $–NH_2$, and then leads to the decline of

absorption capacity. However, the concentration of OH^- is high when pH is higher than 8, and OH^- reacts with Zn^{2+} or Cu^{2+} to form the corresponding precipitations, which causes the decline of absorption capacity.

3. Conclusion

(1) A new amino absorbent has been prepared by crosslinking, hydroxylpropyl chlorination and amination of chitosan. This new absorbent contains much more $–NH_2$, which causes the increase of absorption capacity.

(2) The absorption capacity of chitosan for Zn^{2+} changes little after modification, however, that for Cu^{2+} changes obviously. It's probably because the absorption center in chitosan for Cu^{2+} is $–NH_2$, however, that for Zn^{2+} is –OH.

(3) The absorption capacity of the modified absorbent for Zn^{2+} or Cu^{2+} increases obviously with the rise of temperature.

(4) The absorption capacity increases with the rise of pH at the beginning, and reaches the maximum when pH is 6~7, then decreases with the further increase of pH. It indicates that pH has an obvious effect on the absorption capacity.

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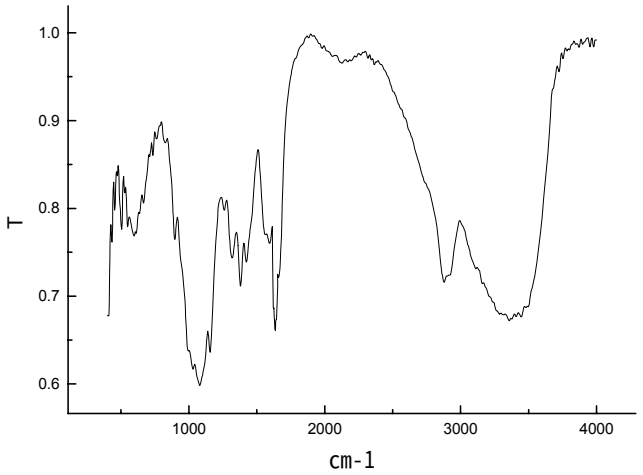
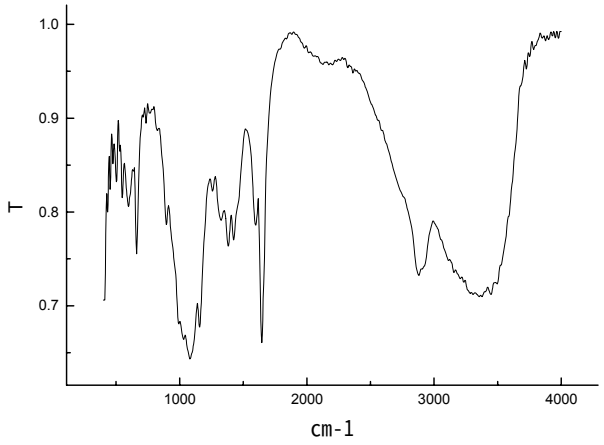
Table 1. Amino contents in chitosan and its derivatives

Products	Amino content (mmol/g)
Chitosan	5.3
Oxaldehyde-modified chitosan	4.2
Epichlorohydrin-modified chitosan	3.9
Monoethylamine-modified chitosan	6.5



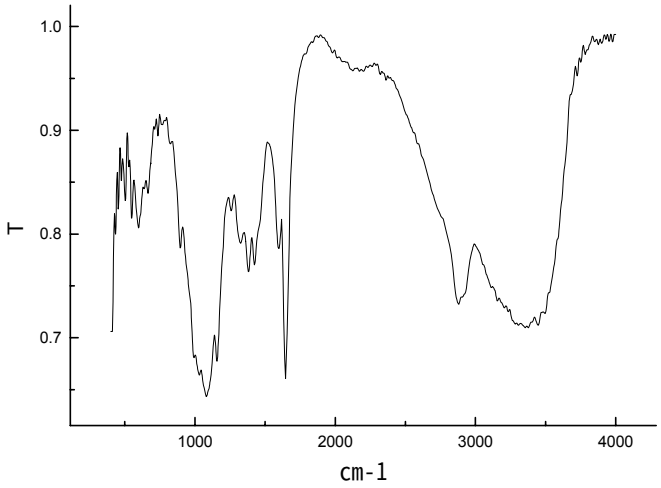
There appear peaks at 3550~3000 cm^{-1} (–OH, $–NH_2$), 1170~1000 cm^{-1} (C–O) and 1660~1680 cm^{-1} (C=N)

Figure 1. IR spectrum of oxaldehyde-crosslinked chitosan



There appear peaks at 3550~3000 cm^{-1} (–OH, $–NH_2$), 1170~1000 cm^{-1} (C–O), 1660~1680 cm^{-1} (C=N) and 690~670 cm^{-1} (C–Cl)

Figure 2. IR spectrum of epichlorohydrin-modified chitosan



There appear peaks at 3550~3000 cm^{-1} (–OH, $–NH_2$), 1170~1000 cm^{-1} (C–O) and 1660~1680 cm^{-1} (C=N)

Figure 3. IR spectrum of monoethylamine-modified chitosan

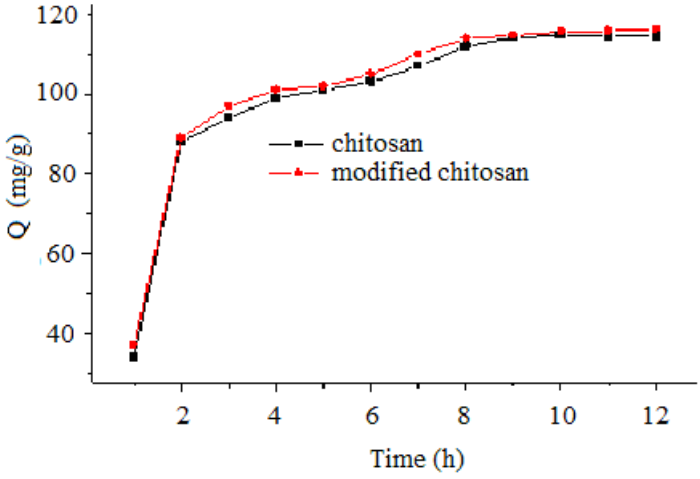


Figure 4. Absorption capacity of chitosan and modified chitosan for Zn^{2+}

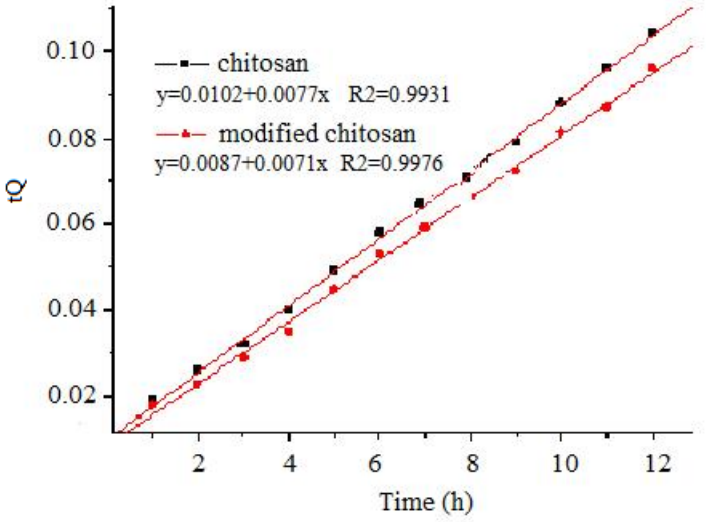


Figure 5. tQ vs. time curve of Zn^{2+}

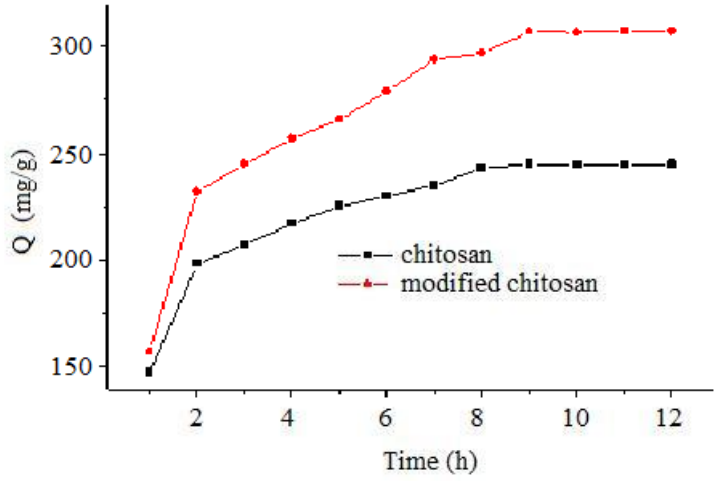


Figure 6. Absorption capacity of chitosan and modified chitosan for Cu^{2+}

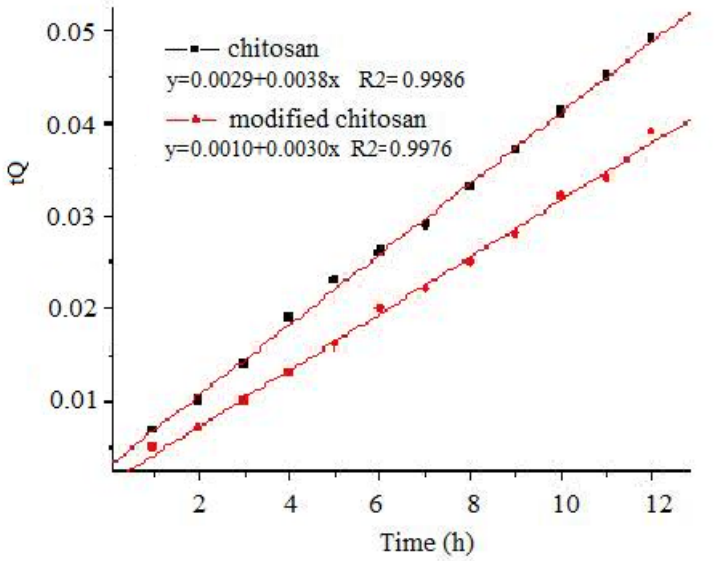


Figure 7. tQ vs. time curve of Cu^{2+}

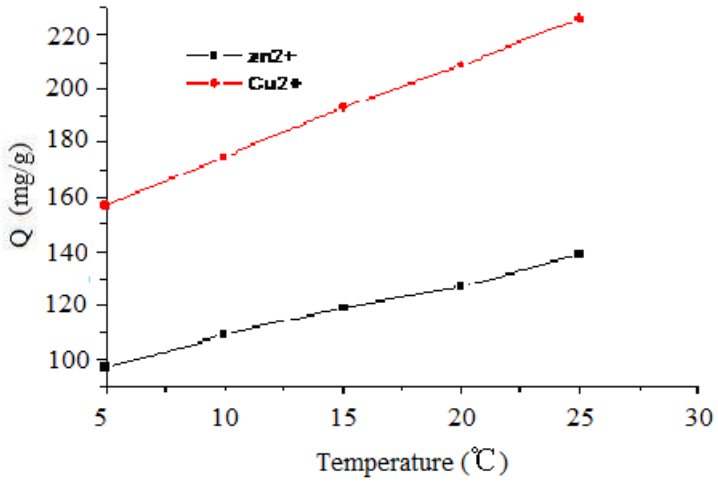


Figure 8. Effect of temperature on absorption of absorbents for Zn^{2+} and Cu^{2+}

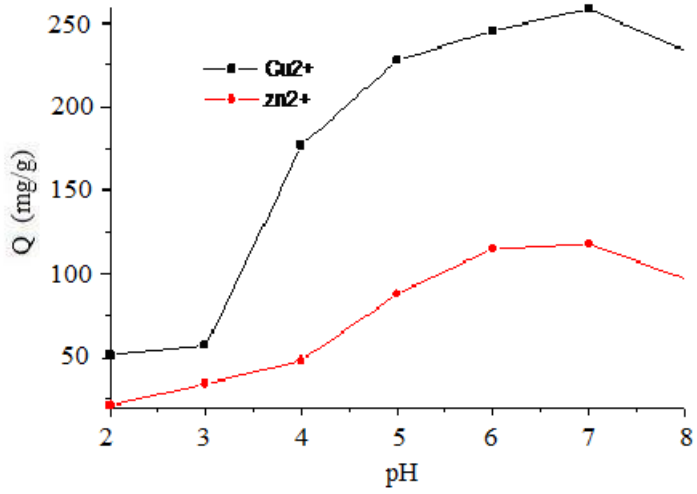


Figure 9. Effect of pH on absorption of absorbents for Zn^{2+} and Cu^{2+}