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Removal of Copper from Aqueous Solutions by Adsorption on Elemental Selenium Nanoparticles

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ABSTRACT: The removal of copper from aqueous solutions using elemental selenium nanoparticles (nanoSe^0) was presented. The uptake of copper by nanoSe^0 depended on reducing agents, such as ascorbic acid (Vc) which reduced Cu(II) to Cu(I). The results of scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX) indicated that nanoSe^0 adsorbed copper by interacting between nanoSe^0 and cuprous ions to form copper selenide (Cu_2Se) on the surface of nanoSe^0. The effects of the mass of nanoSe^0, contact time, pH, initial Cu(II) concentration, and temperature on the removal of copper were investigated. The adsorption kinetics was well-described by the pseudosecond-order equation which suggested that the model was indicative of a chemical adsorption mechanism. The adsorption isotherm was better fitted by the Langmuir equation. The maximum adsorption capacity of nanoSe^0 for copper was found to be 0.89 g·g^{-1} at 298.15 K. The nanoSe^0 coexisting with Vc was a promising adsorbent for the removal copper ions from aqueous solutions. Moreover, the semiconductor materials Cu_2Se could be obtained.

INTRODUCTION

Copper is an essential nutrient in trace quantities but a toxic heavy metal in excess quantities to animals and humans. Copper metals and compounds have wide industrial and commercial applications, and as a result, copper pollution has posed a serious environmental problem due to its toxic effects and accumulation capability throughout the food chain. The continued intake of copper by human beings leads to necrotic changes in the liver and kidney, mucosal irritation, widespread capillary damage, depression, gastrointestinal irritation, and lung cancer.[1] With the increase of industrial activities, copper removal processes have became more and more important. The removal of copper from aqueous solutions has been carried out by techniques such as chemical precipitation,[2] ion exchange,[3] ion flotation,[4] electrolytic methods,[5] reverse osmosis,[6] solvent extraction,[7,8] and adsorption. Chemical precipitation, the electrolytic method, and solvent extraction are only appropriate in the case of concentrated solutions; ion exchange is limited by high operational cost; reverse osmosis requires a high operating pressure, and ion flotation needs abundant surfactants. Adsorption is considered as a powerful technique and extensively used for the removal of copper from domestic and industrial effluent. Activated carbon,[9] metal oxides,[10] clay minerals,[11,12] resins,[13] microbial biomasses,[14,15] chitosan and its derivatives,[16] biosorbents,[17−19] and agricultural waste products[20] have been used as adsorbents for the removal of heavy metal ions from aqueous solutions. However, some of the adsorbents are too expensive or have low adsorption capacity, and other plant materials need pretreatment before use.

Presently the application of nanomaterials, nanoparticles, or nanoadsorbents has emerged as a fascinating area of interest for the removal of metallic pollutants from industrial effluents.[21] Nanosized particles possess a higher adsorption capacity for metal ions than normal-sized ones due to its large surface area.[22,23] In addition, nanoparticles show unique characteristics, such as catalytic potential and high reactivity, which make them good adsorbing materials. Elemental selenium nanoparticles (nanoSe^0) have been regarded as promising materials for many applications due to its unique properties, which include high biological activity, lower toxicity, high particle dispersion, and large surface area.[24,25] It was reported that nanoSe^0 could capture mercury vapor efficiently.[26]

In this paper, we proposed a novel copper removal process by adsorption on nanoSe^0. The major objectives of this study were to: (a) study the function of ascorbic acid and investigate the effects of factors on the removal of copper; (b) determine the adsorption parameters from the adsorption isotherms and the kinetic equations; (c) characterize nanoSe^0 adsorbed with copper and detect the adsorption product; (d) discuss the adsorption mechanisms. The results indicated that the nanoSe^0 coexisting with a proper reducer was a green and efficient adsorbent for the removal of copper from aqueous solutions. Also, the semiconductor materials Cu_2Se could be obtained in the copper removal process.

EXPERIMENTAL SECTION

Materials. Copper sulfate ($CuSO_4 \cdot 5H_2O$), ascorbic acid (Vc), pyrogallic acid (PA), selenious dioxide (SeO_2), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), sucrose, and selenium powder (Se^0 powder) were all analytical grade. Double-distilled water was used throughout the experiment.

The stock solutions of $CuSO_4$ (2000 mg·L^{-1}) were prepared in double-distilled water using copper sulfate. All working solutions were prepared by successively diluting the stock solution with double-distilled water. The solution of Se(IV) was prepared by dissolving SeO_2 in double-distilled water. The

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Table 1. Copper Ion Removal from Aqueous Solutions by Different Elemental Selenium Systems[a]

elemental selenium systems (m_{nanoSe^0} = 0.39 mg, inside the dialysis bag)	$CuSO_4$ solution (outside the dialysis bag)	adsorption capacity ($g \cdot g^{-1}$)
1.0 $mmol \cdot L^{-1}$ nanoSe^0/2 $mmol \cdot L^{-1}$ Vc sol	55.2 $mg \cdot L^{-1}$ Cu(II)	0.32
1.0 $mmol \cdot L^{-1}$ nanoSe^0/30 $mmol \cdot L^{-1}$ Vc sol	55.2 $mg \cdot L^{-1}$ Cu(II)	0.88
1.0 $mmol \cdot L^{-1}$ nanoSe^0/30 $mmol \cdot L^{-1}$ PA sol	55.2 $mg \cdot L^{-1}$ Cu(II)	0.64
1.0 $mmol \cdot L^{-1}$ metastable nanoSe^0 sol	55.2 $mg \cdot L^{-1}$ Cu(II)	—
1.0 $mmol \cdot L^{-1}$ metastable nanoSe^0 sol	55.2 $mg \cdot L^{-1}$ Cu(II) + 30 $mmol \cdot L^{-1}$ Vc	0.84
1.0 $mmol \cdot L^{-1}$ metastable nanoSe^0	55.2 $mg \cdot L^{-1}$ Cu(II) + 30 $mmol \cdot L^{-1}$ PA	0.63
1.0 $mmol \cdot L^{-1}$ nanoSe^0/10% sucrose sol	55.2 $mg \cdot L^{-1}$ Cu(II)	—
1.0 $mmol \cdot L^{-1}$ nanoSe^0/10% sucrose sol	55.2 $mg \cdot L^{-1}$ Cu(II) + 30 $mmol \cdot L^{-1}$ Vc	0.86
1.0 $mmol \cdot L^{-1}$ nanoSe^0/10% sucrose sol	55.2 $mg \cdot L^{-1}$ Cu(II) + 30 $mmol \cdot L^{-1}$ PA	0.62
3.9 mg Se^0 powder	55.2 $mg \cdot L^{-1}$ Cu(II)	—
3.9 mg Se^0 powder	55.2 $mg \cdot L^{-1}$ Cu(II) + 30 $mmol \cdot L^{-1}$ Vc	—

[a] Experiment conditions: pH = 3, time = 12 h, T = 298.15 K. — indicates that the adsorption capacity is nondetectable.

solutions of Vc were prepared freshly. The dialysis bag was boiled in the double-distilled water with ethylenediaminetetraacetic acid (EDTA) for 30 min and stored at 277.15 K in the refrigerator. It was washed by distilled water before use.

Preparation of NanoSe^0 Sols. NanoSe^0-Vc sol was prepared by the reduction of Se(IV) with Vc, following our patented procedure.[27]

Metastable nanoSe^0 sol was prepared by placing the nanoSe^0-Vc sol into the dialysis bag and followed by dialyzing against distilled water for two days to separate Vc from the nanoSe^0 until no ultraviolet absorption of Vc could be found.

NanoSe^0-sucrose sol and nanoSe^0-PA sol were prepared by the reduction of Se(IV) with Vc (1:2 in molar ratio) mixed with appropriate amounts of sucrose and PA.[28]

Uptake Experiment. A dialysis bag containing 5.0 mL of 1.0 $mmol \cdot L^{-1}$ nanoSe^0/30 $mmol \cdot L^{-1}$ Vc sol (m_{nanoSe^0} = 0.39 mg) was placed in a 50 mL container in contact with 25.0 mL of $CuSO_4$ solution at the desired concentration for 12 h. It was crucial to cover the dialysis bag with $CuSO_4$ solution. The dialysis process was that the nanoSe^0 sol in the dialysis bag was adsorbed with the copper ions which could go through the dialysis bag.

The pH values of the $CuSO_4$ solution were adjusted with negligible volumes of (3.0 or 0.1) $mol \cdot L^{-1}$ H_2SO_4 or NaOH. The final pH values of the $CuSO_4$ solution outside the dialysis bag were determined by directly inserting a pH electrode into the $CuSO_4$ solution in the container.

The initial Cu(II) and the final total Cu (Cu(II) and Cu(I)) concentrations outside of the dialysis bag were determined by an atomic absorption spectrophotometer (model: TAS-900 Beijing General Instrument Co., China). The adsorption capacity of the adsorbent (nanoSe^0) was calculated from the following formula:

$$Q = \frac{(C_i - C_t)V}{m} \qquad (1)$$

where Q ($g \cdot g^{-1}$) is the adsorption capacity of the adsorbent and C_i and C_t ($g \cdot L^{-1}$) are the initial Cu(II) and the final total Cu concentrations in the solution, respectively; V (L) and m (g) are the volume of the solution and the dose of the adsorbent, respectively.

Using data from the blank tests, the amount of copper ions inside the dialysis bag was deducted.

The temperature was maintained at 298.15 K for all studies. All of the experimental data were the average of three times duplicate experiments and determination. The relative errors of the data measurements were about 5 %.

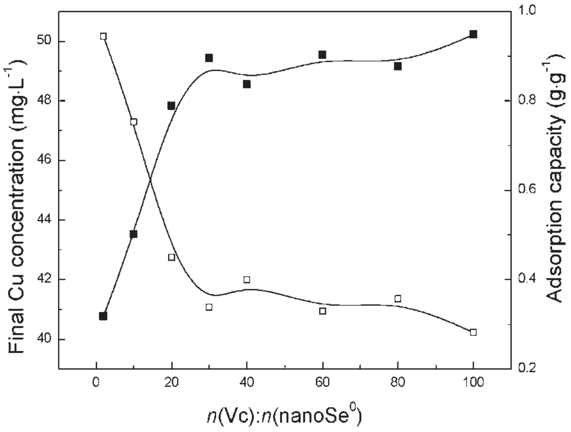


Figure 1. Variation of final Cu concentration and adsorption capacity of nanoSe^0 with the ratio of Vc to nanoSe^0. □, final Cu concentration ($mg \cdot L^{-1}$); ■, adsorption capacity of nanoSe^0 ($g \cdot g^{-1}$). Experiment conditions: m_{nanoSe^0} = 0.39 mg, pH = 3, time = 12 h, T = 298.15 K, $C_{\text{Cu(II)initial}}$ = 55.2 $mg \cdot L^{-1}$.

Characterization. The morphology of the nanoSe^0 adsorbed with copper was observed by scanning electron microscopy (SEM; model: XL-30E, Philips, Germany). The X-ray diffraction (XRD) patterns of nanoSe^0 and nanoSe^0 adsorbed with copper were acquired from 2θ = 10° to 80° using Cu Kα1 radiation (model: MSAL XD-2, Beijing University, China). The accelerating voltage and applied current were 36 kV and 20 mA, respectively. The elemental composition of adsorption product was employed to examine by energy dispersive X-ray analysis (EDX; model: EX-250, Horiba).

■ RESULTS AND DISCUSSION

To study the factors on adsorption capacity, we varied several experimental parameters such as the amount of Vc, adsorption time, the mass of nanoSe^0, pH, and the initial concentration of copper and temperature. SEM, EDX, and XRD were used to characterize the adsorption product.

Copper Adsorbed on NanoSe^0. As listed in Table 1, different elemental selenium systems are used to remove copper in aqueous solution. Experimental results indicated that almost no copper was removed by metastable nanoSe^0 sol and nanoSe^0-sucrose sol, while significant amounts of copper could be

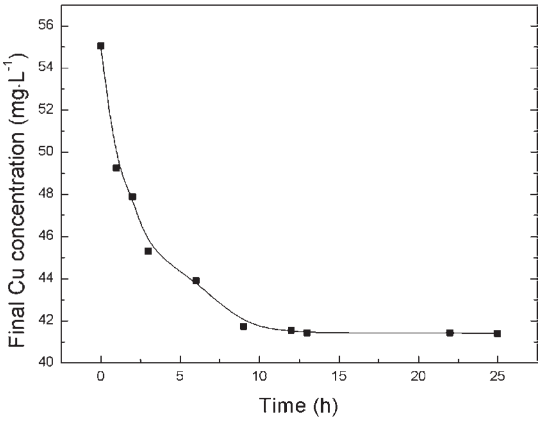


Figure 2. Relationship between the final total Cu concentration and dialysis time. Experiment conditions: m_{nanoSe^0} = 0.39 mg, $n(\text{Vc})/n(\text{nanoSe}^0)$ = 30:1, pH = 3, T = 298.15 K, $C_{\text{Cu(II)initial}}$ = 55.2 mg·L^{-1}.

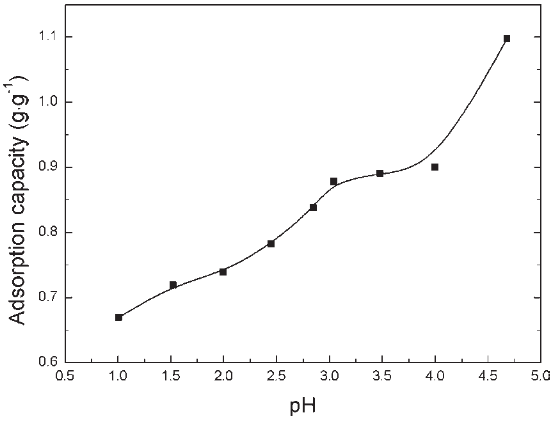


Figure 4. Effect of pH on adsorption capacity of nanoSe^0 for copper. Experiment conditions: m_{nanoSe^0} = 0.39 mg, time = 12 h, T = 298.15 K, $C_{\text{Cu(II)initial}}$ = 55.2 mg·L^{-1}, $n(\text{Vc})/n(\text{nanoSe}^0)$ = 30:1.

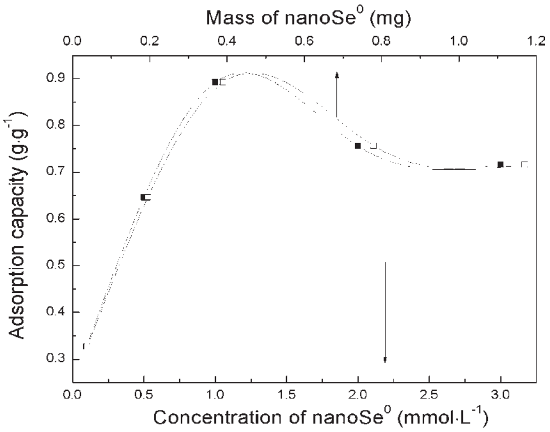


Figure 3. Effect of the concentration and mass of nanoSe^0 on adsorption capacity for copper. ■, concentration; □, mass. Experiment conditions: $n(\text{Vc})/n(\text{nanoSe}^0)$ = 30:1, time = 12 h, pH = 3, T = 298.15 K, $C_{\text{Cu(II)initial}}$ = 55.2 mg·L^{-1}.

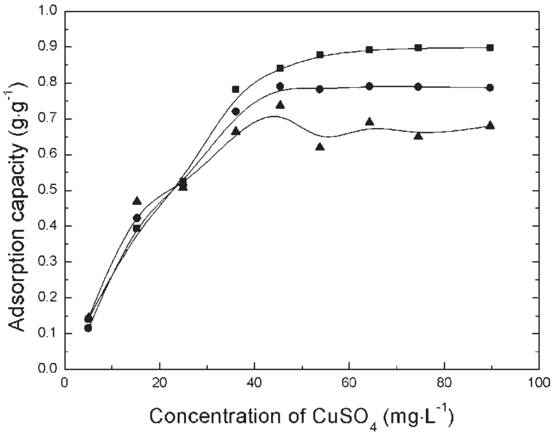


Figure 5. Effect of initial $CuSO_4$ concentration on adsorption capacity of nanoSe^0 for copper at different temperatures. Experiment conditions: m_{nanoSe^0} = 0.39 mg, C_{Vc} = 30 mmol·L^{-1}, time = 12 h, pH = 3. ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K.

removed by nanoSe^0-Vc sol. Also, when 30 mmol·L^{-1} Vc was added into the $CuSO_4$ solution, the copper could be removed by metastable nanoSe^0 sol and nanoSe^0-sucrose sol. However, the Se^0 powder was not able to remove copper.

The effect of Vc quantity on the removal of copper was investigated. As can be seen from Figure 1, the final total Cu concentration decreased as the amount of Vc increased in the range of molar ratio of Vc to nanoSe^0 from 2:1 to 30:1. The result indicated that highly concentrated Vc could not only convert nanoSe^0 to stabilized nanoSe^0-Vc sol[27,28] but also reduce Cu(II) to Cu(I). Other reducers, like pyrogallic acid that was also used as a modifier, could give similar results. Aqueous cuprous ions are always unstable except for forming cuprous insolubles and complexes. The Cu(I) could deposit on the surface of nanoSe^0 through chemical adsorption. Therefore, the nanoSe^0 could act as an adsorbent for copper by the interaction between nanoSe^0 and Cu(I) reduced by the proper reducing agent. Furthermore, some modifiers, like sucrose, did not inhibit nanoSe^0 from adsorbing copper. In this study, nanoSe^0-Vc sol (30:1 in the molar ratio of Vc to nanoSe^0) was used for the following experiments.

Adsorption Equilibrium. The relationship between the final total Cu concentration and the dialysis time is presented in Figure 2. The final total Cu concentration first rapidly decreased within 5 h, then slowly decreased from (5 to 12) h, and finally remained unchanged after 12 h. Obviously, the adsorption equilibrium time was 12 h, so that 12 h was chosen as the dialysis time.

Effect of the Mass of NanoSe^0. The effect of the mass of nanoSe^0 on adsorption capacity is shown in Figure 3. When the mass of nanoSe^0 was changed from 0.039 mg to 1.17 mg, the adsorption capacity of nanoSe^0 for copper increased first and then decreased. Under high concentrations of nanoSe^0, the nanoSe^0 tended to agglomerate into large particles which were less efficient for adsorbing copper. Therefore, 0.39 mg was chosen as the optimum mass of nanoSe^0 when the initial Cu(II) concentration was 55.2 mg·L^{-1}.

Effect of pH. When the dialysis bag was in contact with the $CuSO_4$ solution, the pH of $CuSO_4$ solution changed owing to the diffusion of protons between the nanoSe^0-Vc sol in a dialysis bag and $CuSO_4$ solution. The effect of pH of the solution on adsorption capacity of nanoSe^0 for copper was investigated. As can be seen from Figure 4, it is noteworthy that the adsorption capacity of nanoSe^0 increased with increasing the pH from 1 to 3, which resulted from the electrostatic attraction between positively charged copper ions (Cu(II), Cu(I)) and negatively charged nanoSe^0-Vc sol in which the zeta potential was −34.2 mV at

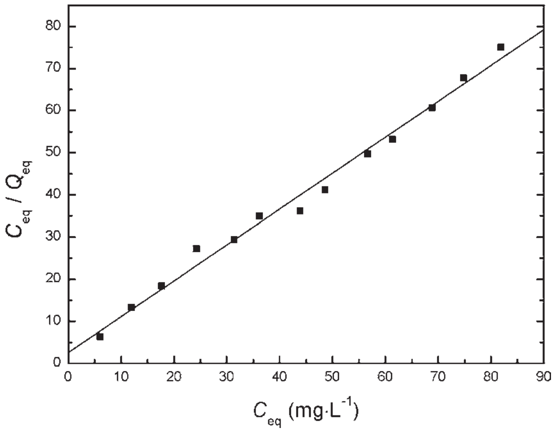


Figure 6. Linearization of the Langmuir adsorption isotherm.

pH 3. As the pH increased, negative charges of the adsorbent surface increased, and the electrostatic attraction between nanoSe^0 and copper ions was likely to be increased. However, Cu(II) ions in aqueous solution could hydrolyze to form Cu(II) hydroxide precipitation above pH 4.5 from our experiment. Therefore, pH 3 was chosen the final pH value of solution outside the dialysis bag.

Effect of Initial Cu(II) Concentration and Temperature. The dependences of adsorption capacity for copper on initial Cu(II) concentrations and experimental temperature are given in Figure 5, which shows that the adsorption capacity decreased obviously at high initial Cu(II) concentrations (in the range of (40 to 88) mg·L^{-1}), whereas they were relatively unchanged at low initial Cu(II) concentrations (< 30 mg·L^{-1}) when raising the temperature. The exact reason for this apparent difference in temperature and concentration dependencies of adsorption capacity is unknown at this time. The obvious decrease of the saturation adsorption capacity when raising the temperature may be related to the desorption of copper on the nanoSe^0 surface. The result revealed that the saturation adsorption (Q_o) was proportional to $1/T$ ($Q_o = -2.34 + 965.86/T$, $R^2 = 0.999$). However, the results at $T = 318.15$ K was high dispersion, which resulted from the unsteadiness of nanoSe^0, and thus the high temperature was a disadvantage for the adsorption on nanoSe^0.

Adsorption Isotherms. To design the adsorption process, it is useful to employ mathematical models to predict the metal adsorption. The Langmuir equation was applied to quantify adsorption capacity and is given as follows:[29]

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q_0 b} + \frac{C_{eq}}{Q_0} \tag{2}$$

where Q_{eq} (g·g^{-1}) is the adsorption capacity at equilibrium, C_{eq} (mg·L^{-1}) is the concentration of copper ions in the aqueous phase at equilibrium, Q_0 (g·g^{-1}) is the saturation adsorption, and b (L·mg^{-1}) is the Langmuir constant. Hence, a plot C_{eq}/Q_{eq} versus C_{eq} should be a straight line with a slope $1/Q_0$ and intercept as $1/Q_0b$.

The linearization of the equation was shown in Figure 6. The linear curve ($R^2 = 0.990$) obtained resulted in the following equation:

$$\frac{C_{eq}}{Q_{eq}} = 2.55 + 1.12C_{eq} \tag{3}$$

The intercept of this equation represented the $1/Q_0b$, and the slope corresponded to the $1/Q_0$. The value for the Q_0 was 0.89 g·g^{-1}, and the Langmuir constant b was 0.44 L·mg^{-1} at $T = 298.15$ K, while the results obtained from the Freundlich model (not shown) presented a poor linear fit for copper. This equation suggested that the Langmuir model was a good interpretation of the experimental data.

Adsorption Kinetics. To evaluate the mechanism of the adsorption kinetics, the pseudofirst-order, pseudosecond-order, and intraparticle diffusion models[30] were tested to interpret the experimental data. The pseudofirst-order kinetics model is given below:

$$\log(Q_{eq} - Q_t) = \frac{\log Q_{eq} - k_1 t}{2.303} \tag{4}$$

The pseudosecond-order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q_{eq}}^2} + \frac{t}{Q_{eq}} \tag{5}$$

The intraparticle diffusion rate can be described as:

$$Q_t = k_i t^{1/2} \tag{6}$$

where Q_t is the adsorption capacity in time t (g·g^{-1}), Q_{eq} the adsorption capacity at equilibrium (g·g^{-1}), and k_1, k_2, and k_i are the adsorption rate constant of pseudofirst-order (h^{-1}), pseudosecond-order (g·g^{-1}·h^{-1}), and intraparticle diffusion rate (g·g^{-1}·h$^{-1/2}$), respectively. The validity of these models can be interpreted by the linear plots of $\log(Q_{eq} - Q_t)$ versus t, (t/Q_t) versus t, and Q_t versus $t_{1/2}$, respectively.

As can be seen from Figure 7a to c, the correlation coefficients (R^2) calculated by the three kinetic models were 0.953, 0.996, and 0.790, respectively. On the basis of the obtained correlation coefficients, the pseudosecond-order equation was the best fit for the experimental kinetic data. The rate constant k_2 determined was 2.02 g·g^{-1}·h^{-1}. The pseudosecond-order model suggested that the rate-limiting step may be the chemical adsorption not the mass transport limitation.[31,32]

XRD, SEM, and EDX. The XRD pattern of nanoSe^0 adsorbed with copper is different from nanoSe^0. There were two obvious diffraction peaks at 26.7° and 44.8° in Figure 8b which are the typical diffraction peaks of the Cu_2Se phase according to the Joint Committee on Powder Diffraction Standards (JCPDS) file 88-2043. It indicated that a part of nanoSe^0 converted to Cu_2Se after copper adsorption.

The SEM images of nanoSe^0-Vc sol dialyzing against water and $CuSO_4$ solution are shown in Figure 9. There was no obvious difference between nanoSe^0 and nanoSe^0 adsorbed with copper in the morphology and apparent size. The results indicated that Cu_2Se formed at the nanoSe^0 surface have not changed the morphology of nanoSe^0.

Figure 10 shows the EDX spectrum of nanoSe^0 adsorbed with copper. The elemental analysis result showed that the atomic ratio of Cu to Se was to 2.6:1 which was a little different from the result of XRD (2:1). The C atom signal (24.24 %) and the O atom signal (3.12 %) were due to the presence of Vc which was still present in the particles. The atomic ratio of Cu to Se was higher than the stoichiometry of Cu_2Se due to the electrostatic attraction between copper ions and nanoSe^0-Vc sol.

Removal Mechanism of Copper. The removal process of copper from aqueous solutions was proposed as follows: the reductive Vc diffused from the inside of a dialysis bag to outside, while Cu(II) diffused from the outside to inside and Vc reduced Cu(II) to Cu(I). Then Cu(II) and Cu(I) adhered on the surface

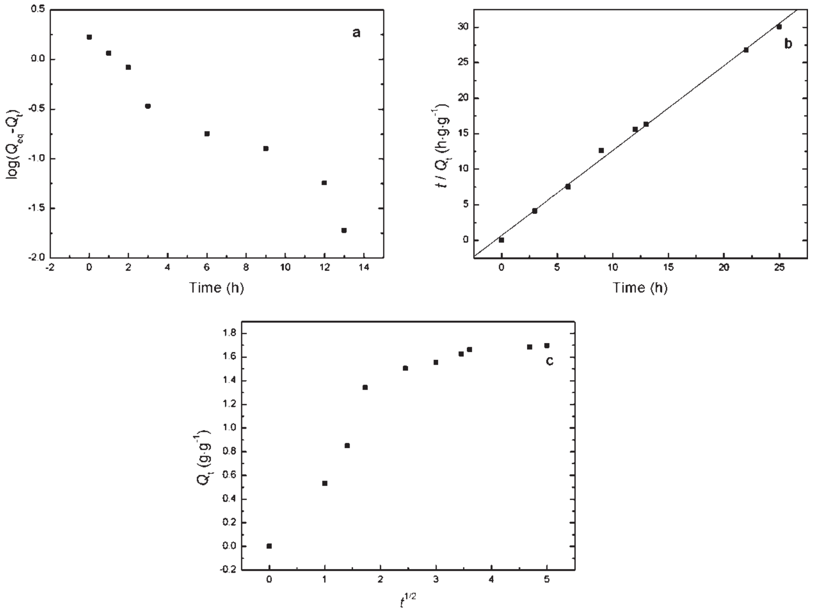


Figure 7. Linearization of adsorption kinetics. (a) Pseudofirst-order model, (b) pseudosecond-order model, and (c) intraparticle diffusion model.

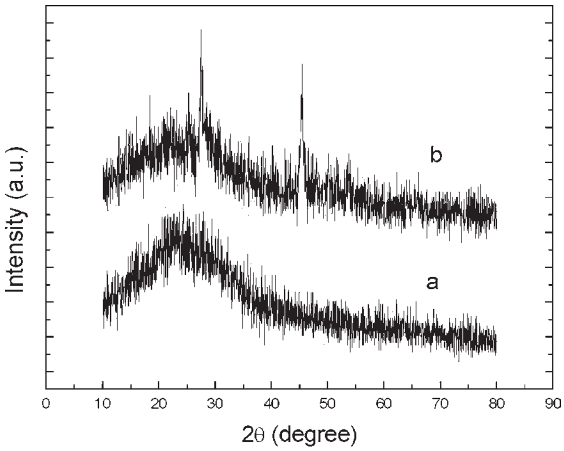


Figure 8. XRD patterns of the nanoSe^0 (a) before and (b) after copper adsorbed.

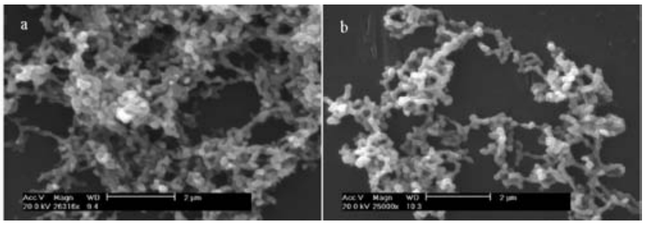
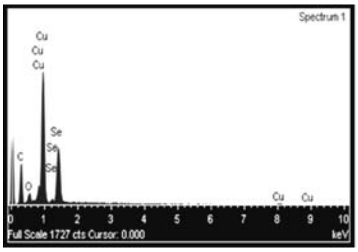


Figure 9. SEM images of the nanoSe^0-Vc sol dialyzed against water (a) and 55.2 mg·L^{-1} $CuSO_4$ solution (b) for 12 h at T = 298.15 K.

of negatively charged nanoSe^0 by the electrostatic attraction. Finally, the nanoSe^0 reacted with Cu(I) within a dialysis bag to form Cu_2Se on the surface of nanoSe^0. The removal process was mainly controlled by chemical adsorption.



Element	Weight%	Atomic%
C	24.24	61.45
O	3.12	5.94
Cu	49.11	23.53
Se	23.53	9.07
Totals	100.00	

Figure 10. EDX spectrum of Cu_2Se.

The chemical reaction mechanism could be described as follows:

$$\mathrm{Cu(II)_{aq}} + \text{reductive Vc} \rightarrow \mathrm{Cu(I)_{aq}} + \text{oxidative Vc}$$

$$\mathrm{nanoSe^0_{sol}} + 2\mathrm{Cu(I)_{aq}} \rightarrow \mathrm{Cu_2Se_{nanoSe^0surface}}$$

Cu(I) could be disproportionate to Cu(II) and Cu(0). The Cu(0) also could react with nanoSe^0.[33]

CONCLUSIONS

The removal of copper ions by nanoSe^0 depended on the proper reducing agents (such as Vc and PA) which could reduce Cu(II) into Cu(I). Aqueous cuprous ions are always unstable except when forming cuprous insolubles and complexes. The Cu(I) could be deposited on the surface of nanoSe^0 to form Cu_2Se through chemical adsorption. The adsorption product (Cu_2Se) had not changed the morphology of nanoSe^0. The amount of Cu(II) adsorbed depended on the mass of nanoSe^0, contact time, and pH. The final equilibrium depended on the initial Cu(II) concentration, and the adsorption capacity depended on temperature. The adsorption in the uptake process followed the Langmuir isotherm, and the kinetics mechanism followed the pseudosecond-order model. The maximum adsorption capacity of the nanoSe^0 for copper was 0.89 g·g^{-1} at 298.15 K. The nanoSe^0 coexisting with a proper reducer was proven to be a suitable adsorbent for the removal of copper from aqueous solutions because of its lower toxicity, high particle dispersion, and large surface area. The semiconductor materials Cu_2Se could be obtained in the copper removal process.

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