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Adsorption removal of Congo red from aqueous solution by polyhedral Cu₂O nanoparticles: Kinetics, isotherms, thermodynamics and mechanism analysis



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ABSTRACT

Polyhedral cuprous oxide nanoparticles (Cu₂O NPs) with rough surfaces were prepared by a one-pot sonochemical precipitation method. The products were characterized by SEM, XRD, EDS, XPS, and UV–Vis DRS, respectively. The adsorption behavior of Congo red (CR) from aqueous solution onto the as-prepared Cu₂O NPs was systematically investigated. The equilibrium and kinetic studies suggested that the adsorption process followed Freundlich isotherm and pseudo-second order model, respectively. The as-prepared Cu₂O NPs exhibited remarkable adsorption properties toward CR. The maximum adsorption capacity at 20 °C was 3904 mg g⁻¹, which was the highest reported value so far in adsorption removal of CR. Together with the evaluation of the thermodynamic parameters such as Gibbs free energy, enthalpy and entropy change, our results show that the adsorption of CR onto Cu₂O NPs was proposed. Moreover, the Cu₂O adsorbent could be photocatalytically regenerated and reused without significant loss of its adsorption capability.

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1. Introduction

Congo red (CR) is a benzidine-based anionic diazo dye, which contains one central biphenyl group and two symmetric naphthalenic groups (Fig. 1). CR is widely used in textile, paper, printing, leather and plastic industries [1,2]. It is also used as a laboratory aid for testing free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as a pH indicator and a histological stain for amyloid [3]. However, CR is an irritant to skin and eye, and induces somnolence and respiratory problems [3]. Furthermore, CR has also been known to cause an allergic response and to be metabolized to benzidine, a well-known human carcinogen [4]. Therefore, the removal of CR from wastewater effluents before mixing with unpolluted natural water bodies is of environmental significance [5,6].

To purify wastewater contaminated by CR, various techniques including adsorption [3], photodegradation [7], chemical oxidation [8], coagulation [9], electrochemical oxidation [10] and

microbiological treatment [11] have been employed. Among these techniques, adsorption has been intensively concerned and found to be superior to other techniques due to its simple operation, high efficiency, economy and convenience. A number of adsorbents, including activated carbon [12], acid activated red mud [13], fly ash [14], clay materials (such as montmorillonite [15], bentonite [2] and zeolite [2]), biomaterials (such as peanut hull [16], orange peel [17] and rice husk [1]), inorganic metal oxides (such as ZnO [18], $Fe_{3-x}La_xO_4$ ferrite [19] and γ -Fe₂O₃ modified TiO₂ [20]) as well as polymers [21] have been studied for CR removal. These adsorbents described above usually suffer from some disadvantages, such as high cost, low adsorption capacity, multi-step synthesis procedures, or inability to regenerate and recycle. Therefore, it is very necessary to develop new adsorption materials with low cost, high adsorption capacity, as well as regenerative and recyclable properties.

As an abundant and nontoxic material, cuprous oxide (Cu₂O) is a *p*-type semiconducting material with a direct band gap of about 2.17 eV [22], which has been widely applied in many fields, including gas sensors, lithium ion batteries, solar energy conversion, photocatalytic degradation of organic pollutants and magnetic storage



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[23–25]. In addition, Cu₂O has also been used for the adsorption removal of some organic dyes such as acid orange II [26] and methyl orange [27] from wastewater. However, a systematic study on the adsorption behavior of CR onto Cu₂O nanoparticles (Cu₂O NPs) has not yet been reported. In this work, polyhedral Cu₂O NPs with rough surfaces were prepared by a one-pot sonochemical precipitation method for use as an adsorbent. The kinetics, isotherms, thermodynamics and mechanism of CR adsorption onto Cu₂O NPs were systematically studied and discussed. The Cu₂O NPs adsorbent demonstrated unprecedented removal capability and showed the highest adsorption capacity toward CR compared to previously reported adsorbents. Moreover, the Cu₂O adsorbent could be regenerated photocatalytically and reused without significant loss of its adsorption capability, indicating its potential for the removal of CR from aqueous solution.

2. Experimental

2.1. Materials

Copper sulfate pentahydrate (CuSO₄·5H₂O), sodium hydroxide (NaOH), ascorbic acid, hydrogen chloride (HCI) and Congo red (CR) were purchased from Chendu Kelong Chemical Reagent Company (China) and used as received. Deionized water was used in all experiments.

2.2. Preparation of polyhedral Cu₂O NPs

Cu₂O NPs were prepared by the reduction of Cu(II) with ascorbic acid in alkaline conditions. Typically, 56 mL NaOH solution (1.5 mol L⁻¹) was added dropwise into 28 mL CuSO₄ solution (0.5 mol L⁻¹) under ultrasonication and magnetic stirring. The resulting solution turned light blue immediately, indicating the formation of Cu(OH)₂ precipitate. Then 50 mL of freshly prepared ascorbic acid solution (0.1 mol L⁻¹) was immediately added dropwise to the above suspension. The resulting mixture was then ultrasonicated and stirred for another 1 h. Finally, the red precipitate was collected by filtration, washed repeatedly with deionized water until the pH of the aqueous effluent was neutral, and dried at 60 °C in an oven.

2.3. Characterization

The crystal structure and phase purity were determined by X-ray diffraction (XRD) technique using a Rigaku Dmax/Ultima IV X-ray diffractometer equipped with monochromatized Cu K α radiation (λ = 1.5418 Å). Morphology was analyzed using scanning electron microscope (Hitachi S4800). Energy dispersive X-ray spectroscopy (EDS) was measured by using an energy dispersive X-ray spectrometer (Oxford instrument X-Max). The oxidation states of ions were determined from X-ray photoelectron spectroscopy (XPS) on a Kratos XSAM800 XPS spectrometer equipped with Al K α excitation source (1486.6 eV). All XPS spectra were corrected using the C 1s line at 284.8 eV. The optical band gap was estimated from UV–Vis diffuse reflectance spectroscopy (DRS) using a Shimadzu UV-3600 spectrophotometer. Fourier Transform Infrared (FTIR) spectra were recorded with KBr pellets on a Nicolet 6700 FTIR spectrometric analyzer.

2.4. Adsorption experiments

Batch adsorption experiments were carried out by adding 50 mg Cu₂O NPs to 50 mL CR solution on a thermostatic incubator shaker with a shaking speed of 150 rpm at 30 °C, unless otherwise stated. In pH studies, the CR concentration was 300 mg L⁻¹, and the pH of the CR solutions was adjusted with 0.1 M HCl or 0.1 M NaOH. In adsorption kinetic experiments, the concentrations of CR solution ranged from 300 to 1000 mg L⁻¹ in natural pH conditions (the pH values were near neutral). For adsorption isotherm and thermodynamic studies, the CR concentrations ranged from 750 to 6000 mg L⁻¹ in natural pH conditions and at different tem-



Fig. 1. Molecular structure of Congo red.

peratures (20–40 °C). All mixtures after adsorption experiments were centrifuged to yield clear supernatant solutions. The concentration of the residual CR dye in the supernatant solution was measured by UV–Vis spectroscopy (UV-2550, Shi-madzu) at the maximum absorbance of CR dye (496 nm) on the basis of Beer–Lamber law. Unless otherwise stated, all the experiments were performed twice, and the mean values were presented with error less than 5%.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 2a shows a typical SEM image of the as-prepare Cu₂O sample. One can see that the Cu₂O sample is composed of a large guantity of uniform particles with polyhedralmorphology (truncated octahedra). The size of the polyhedral structures is mainly in the range of 300–500 nm. The high-magnification SEM image in Fig. 2b reveals that the surfaces of the Cu₂O are rather rough. Many holes, crevices and small particles (indicated by arrows) can be observed on the surfaces of the Cu₂O NPs. Fig. 2c depicts the XRD pattern of the as-prepared Cu₂O sample. All the diffraction peaks of the Cu₂O sample are labeled and can be indexed very well to the standard cubic phase of Cu₂O with lattice constant a = 4.2696 nm (JCPDS No. 05-0667). Diffraction peaks corresponding to impurities such as CuO and Cu are not detected in the XRD patterns, indicating that the as-prepared products exist mainly as Cu₂O phase. The EDS analysis also shows that the atomic ratio of copper to oxygen is close to 2:1 (Fig. 2d), confirming that the asprepared products are Cu₂O crystals.

Fig. 3a shows the XPS spectra of Cu 2p of the as-prepared Cu₂O sample. Shake-up features at about 943 and 963 eV (denoted by arrows) for Cu $2p_{3/2}$ and $2p_{1/2}$ core levels verify the open $3d^9$ shell of Cu(II) [28,29]. The peaks centered at 932.4 and 952.2 eV can be assigned to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu(I) [30], while the peaks centered at 934.8 and 954.5 eV are attributed to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu(II) [28,31]. The binding energy at 934.8 eV for Cu(II) is higher than the previously reported values of CuO in the range of 933.4–933.9 eV [32]. It has been reported that when the content of CuO is low, the binding energies of Cu(II) will shift to higher values [33]. Thus the binding energy of CuO at 934.8 eV in our sample may be due to the small content of CuO on the sample surfaces.

Fig. 3b shows the O 1s core-level XPS spectrum. There is a broad peak centered at about 531 eV, and it can be further divided into three peaks through a curve fitting procedure. According to previous studies, the peak at 530.5 eV is in agreement with the lattice oxygen in Cu₂O [32,34], the peak at 531.8 eV can be assigned to the presence of hydroxyl groups adsorbed on the surface of Cu₂O [31,34–36], while the O 1s peak at the higher energy (533.8 eV) is associated to the O^{2-} of water adsorbed on the surface of Cu₂O [37].

The UV-Vis diffused reflectance spectrum (DRS) of the as-prepared Cu₂O NPs exhibits a broad absorption band in the visible region (Fig. 4a), which is attributed to the overlap of the band gap absorption and the light scattering effect due to the relatively large size (compared to Cu₂O nanoparticles with sizes of around 100 nm or less [38]). Two absorption peaks (\sim 450 and \sim 550 nm) of the intrinsic band absorption in the range of 400-600 nm are observed, although they are generally weak [39]. The direct optical band gap energy (E_g) was estimated from the plot of $(\alpha E_p)^2$ versus E_{p} , where α and E_{p} are the absorption coefficient and the discrete photo energy [39,40]. The E_g was determined by extrapolating the linear portion of the curve to zero [40]. The estimated value is 1.99 eV for the as-prepared Cu₂O NPs (Fig. 4b). This value is smaller than that of bulk Cu₂O particles (2.17 eV [22]), but slightly greater than some of the reported values (1.93-1.97 eV [39,41]). The band gap differences may be caused by the morphology effect of Cu₂O particles [41].



Fig. 2. Typical SEM images (a and b), XRD pattern (c) and EDS spectrum (d) of the as-prepared Cu₂O NPs.



Fig. 3. XPS spectra of (a) Cu 2p and (b) O 1s of the sample.



Fig. 4. The UV–Vis diffused reflectance spectrum (DRS) of the as-prepared Cu₂O NPs (a) and band gap estimation from the plot of $(\alpha E_p)^2$ versus E_p (b).

3.2. Effect of pH

Fig. 5 displays the effect of pH on the removal of CR. The removal percentage of CR slightly increases from 81% to 86% when the pH increases from 5 to 7, and then decreases from 86% to 70% with an increase in solution pH from 7 to 11. Two possible mechanism of CR adsorption onto Cu₂O may be considered: electrostatic interaction and chemical reaction between the adsorbate and the adsorbent. At lower pH, strong electrostatic attraction may exist between the positively charged surface of Cu₂O and the negatively charged sulfonic acid group of CR dye. At higher pH, the number of positively charged sites decreases and negatively charged sites increases. A negatively charged surface does not favor the adsorption of dye anions due to electrostatic repulsion. At the same time, the presence of excess OH⁻ at higher pH conditions will compete with the dve anions for the adsorption sites. It has been reported previously that the removal percentage of CR onto magnetic cellulose/Fe₃O₄/activated carbon composites (m-Cell/Fe₃O₄/ACCs) continuously decreases from 83.4% to 14.1% with an increase in pH from 4 to 9.5 due to the electrostatic attraction and electrostatic repulsion between CR anions and the surfaces of the adsorbent at different pH conditions [42]. In our case, significant adsorption of CR onto the Cu₂O adsorbent still occurs at alkaline pH conditions, suggesting that chemisorption may be involved in the adsorption process.

3.3. Effect of contact time and initial dye concentration

Fig. 6 shows the effect of contact time on the adsorption capacity and removal percentage of CR onto Cu_2O NPs. Both adsorption capacity and removal percentage show rapid increase with contact time in the initial adsorption stage (the first 12 h). Then the adsorption presents a relatively slow increase until it closes to equilibrium state in about 22 h. The adsorption capacity and removal percentage of CR only increase slightly with increase in contact time for up to 48 h.

Besides contact time, the adsorption is also influenced by the initial CR concentration. When the amount of Cu₂O NPs is fixed, the adsorption capacity of CR increases (Fig. 6a), while the removal percentage of CR decreases with the increase of initial CR concentration (Fig. 6b). Indeed, the initial dye concentration provides the necessary driving force to overcome the resistance of the mass transfer from the aqueous phase to the solid phase. On the other hand, adsorption process generally involves the first transport of adsorbate molecules from the bulk solution to the exterior surface of adsorbent and then from the exterior surface to the pores of the adsorbent. Therefore, the increase in initial CR concentration can



Fig. 5. Effect of the solution pH on the adsorption of CR onto Cu₂O NPs.

enhance the interaction between CR and Cu₂O, which results in the increase of adsorption capacity of CR. These results suggest that the amount of CR molecules is not enough to occupy the adsorption sites of the Cu₂O NPs, thus the adsorption is not saturated.

3.4. Adsorption kinetics

The kinetics of CR adsorption onto Cu₂O NPs was studied to understand the characteristics of the adsorption process. Pseudofirst, pseudo-second order and intraparticle diffusion kinetic models were used to describe the adsorption process.

The pseudo-first order model presented by Lagergren [43] is widely used for describing the kinetic process of liquid-solid system on the basis of solid capacity. The linear form can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q_e and q_t (mg g⁻¹) are the amounts of adsorbate adsorbed at equilibrium and at time *t*, respectively. k_1 is the pseudo-first order rate constant.

The pseudo-second order model proposed by Ho and McKay on the basis that the adsorption obeys second order chemisorption [44]. A linear form can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where k_2 is pseudo-second order rate constant. The initial adsorption rate, h_0 , is defined as:

$$h_0 = k_2 q_e^2 \tag{3}$$

The experimental data can be fitted to both pseudo-first (Fig. 7a) and pseudo-second order models (Fig. 7b). The kinetic parameters (q_e , k_1 , k_2 and h_0) and the correlation coefficients (R^2) determined by linear regression are given in Table 1. The R^2 values for pseudo-second order kinetic model at all the concentrations studied are higher than those for pseudo-first order model (Table 1), indicating that the pseudo-second order model is more suitable for describing the adsorption behavior of CR onto Cu₂O NPs. It is also shown in Table 1 that the initial adsorption rate (h_0) increases, while the rate constant (k_2) decreases with the increase in initial CR concentration. A similar phenomenon has been observed in the adsorption of Cu(II) onto chestnut shell [45].

The Weber's intraparticle diffusion model was employed to elucidate the diffusion mechanism and to identify the steps involved in the adsorption process [46]:

$$q_t = k_i t^{1/2} + c \tag{4}$$

where k_i is the intraparticle diffusion rate constant (mg g⁻¹ h^{-1/2}), and *c* is a constant $(mg g^{-1})$ that gives idea about the thickness of the boundary layer. According to the Weber's model, if the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step and the adsorption process is controlled by intraparticle diffusion. Otherwise, two or more steps are involved in the adsorption process [45,46]. As shown in Fig. 7c, the plots of q_t versus $t^{1/2}$ presents multilinearity, indicating that two or more steps take place during the adsorption process. The first sharp linear region is a diffusion adsorption stage. attributing to the diffusion of dye molecules through the solution to the external surface of adsorbent (film diffusion). The second linear region is a gradual adsorption stage, where the intraparticle diffusion is rate-controlled (intraparticle diffusion) [45]. The third region reflects the final equilibrium stage, where intraparticle diffusion begins to slow down due to the lower adsorbate concentration in the solution. The linear plot at each concentration does not pass



Fig. 6. Effect of contact time and initial CR concentration on the adsorption capacity (a) and removal percentage (b) of CR onto Cu₂O NPs.



Fig. 7. Kinetics of CR adsorption onto Cu₂O NPs at 30 °C. Pseudo-first order (a), pseudo-second order (b) and intraparticle diffusion (c) plots.

Table 1
Kinetic parameters for the adsorption of CR onto $\mbox{Cu}_2\mbox{O}$ NPs.

$C_0 ({ m mg}{ m L}^{-1})$	$q_{e,exp} (\mathrm{mg}\mathrm{g}^{-1})$	Pseudo-first-order		Pseudo-second-order				
		$q_{e,cal} (\mathrm{mg}\mathrm{g}^{-1})$	$k_1 ({ m h}^{-1})$	R^2	$k_2 (g m g^{-1} h^{-1})$	$q_{e,cal} (\mathrm{mg}\mathrm{g}^{-1})$	h_0	R^2
300	290	241	0.200	0.969	1.45×10^{-3}	305	134.8	1
600	546	519	0.160	0.985	4.16×10^{-4}	610	154.6	0.999
1000	845	779	0.136	0.990	$\textbf{2.37}\times \textbf{10}^{-4}$	926	203.3	0.999

through the origin, indicating that the intraparticle diffusion is not the only rate controlling step [47].

3.5. Adsorption isotherms

Successful application of the adsorption technique demands studies based on various adsorption isotherm models, because

adsorption isotherm models clearly depict the relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium [48]. In this study, two well-known isotherm models, Langmuir and Freundlich models were employed to analyze the experimental data.

The Langmuir isotherm equation is: [49]

Table 2 Isotherm parameters for CR adsorption onto Cu_2O NPs at different temperature.

Isotherm model	Parameters	Temperature (°C)		
		20	30	40
Langmuir	b q _m R ²	$\begin{array}{c} 1.22\times 10^{-3} \\ 3904 \\ 0.981 \end{array}$	$\begin{array}{c} 2.17\times 10^{-3} \\ 5124 \\ 0.981 \end{array}$	$\begin{array}{c} 2.35\times 10^{-3} \\ 8220 \\ 0.989 \end{array}$
Freundlich	K _F 1/n R ²	31.07 0.61 0.988	43.28 0.66 0.991	63.56 0.69 0.993

Table 3

Thermodynamic parameters for the adsorption of CR onto Cu₂O NPs.

T (K)	K _d	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
293 303 313	4.904 10.591 18.916	-3.87 -5.95 -7.65	51.53	189.28

$$q_e = \frac{bq_m C_e}{1 + bC_e} \tag{5}$$

The linear form can be expressed as [50]:

$$\frac{1}{q_e} = \frac{1}{bq_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{6}$$

The Freundlich isotherm equation is [51]:

$$q_e = K_F C_e^{1/n} \tag{7}$$

The linear form can be expressed as [50]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

where q_m is the Langmuir monolayer adsorption capacity (mg g⁻¹), q_e the amount of CR adsorption at equilibrium (mg g⁻¹), C_e the

The parameters of the adsorption isotherms obtained through linear regression (Fig. S1) are summarized in Table 2. According to the values of correlation coefficients (R^2), the Freundlich model is more suitable than the Langmuir model for describing the adsorption. The maximum adsorption capacity (q_m) is found to increase with rising temperature, indicating that higher temperature facilitates the adsorption of CR onto Cu₂O NPs and the adsorption is an endothermic process. The values of 1/n for the three temperatures studied fall in the range of 0–1, suggesting the favorable adsorption of CR onto the Cu₂O NPs [52]. By comparing with other adsorbents reported previously (Table S1), the Cu₂O NPs adsorbent shows the highest adsorption capacity, suggesting the significant potential of Cu₂O NPs as an adsorbent.

3.6. Adsorption thermodynamics and mechanism

The thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. Thermodynamic parameters such as the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy change (ΔS°) of the adsorption process can be estimated from the following equations:

$$\Delta G^{\circ} = -RT \ln K_d \tag{9}$$

$$\ln K_d = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} \tag{10}$$

where *T*(K) is the absolute temperature and *R*(8.314 J mol⁻¹ K⁻¹) is the gas constant. K_d (L g⁻¹) is the thermodynamic equilibrium constant, which can be calculated by using the method of Khan and Singh, i.e. plotting ln (q_e/C_e) versus q_e and extrapolating q_e to zero [53,54]. The value of ΔG° can be calculated according to Eq. (9),



Fig. 8. (a) Schematic illustration of the exposed {111} and {100} planes of the as-prepared polyhedral Cu₂O NPs, (b) the unit cell of the cuprite Cu₂O, (c) and (d) the atomic arrangement in {100} and ({111} planes of Cu₂O structure, respectively. In panels b–d: Red spheres represent O atom and blue sphere represent Cu atom as shown in panel d. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. Putative interaction model between Congo red and Cu₂O.

and the values of ΔH° and ΔS° can be calculated from the slope and intercept by plotting ln K_d versus 1/T as shown in Fig. S2.

Table 3 summarizes the values of ΔG° , ΔH° and ΔS° . The value of ΔG° is negative and the negative value decreases with rising temperature, suggesting that the adsorption is spontaneous and the adsorption is more favorable at higher temperatures. If adsorption decreases with increasing temperature, it may be indicative of physical adsorption, and the reverse is generally true for chemisorption [55]. In the present work, the increase in adsorption with increasing temperature and slow adsorption kinetics indicate the presence of chemical adsorption. The value of enthalpy (ΔH°) is positive (51.53 kJ mol⁻¹), indicating the endothermic nature of the adsorption process. Endothermic adsorption of some dyes on various adsorbents has also been reported in earlier literatures [12.56]. Generally, an exothermic adsorption process signifies either physical or chemical sorption while endothermic process is attributable unequivocally to chemisorption [55]. Therefore, the positive enthalpy in this study further confirms that the adsorption of CR onto Cu₂O is dominated by chemical adsorption rather than physical adsorption [12]. The positive value of ΔS° $(189.28 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})$ implies that the adsorption of CR onto the Cu₂O NPs increases the randomness in the solid/solution interface. The increase in entropy is probably caused by the release of water molecules into the bulk solution from the solid surface during the adsorption process [12,55].

To examine the interaction between CR and Cu₂O NPs. We measured the FTIR spectra of CR before and after adsorption. The FTIR spectrum of CR before adsorption (Fig. S3, curve a) is consistent with previous reports [57,58]. The peak at 642 cm⁻¹ corresponds to C-C bending vibration, peak at 698 cm⁻¹ to C-H stretching vibration of disubstituted aromatic compound, while the peak at 833 cm^{-1} corresponds to *p*-disubstituted ring vibration, 1062 cm⁻¹ to S=O stretching vibration of sulfonic acid, respectively. Additionally, peak located at 1358 cm^{-1} is from C–N bending vibration mode, peak at 1448 cm⁻¹ from aromatic C=C stretching vibration, while peak at 1585 cm⁻¹ comes from N=N stretching vibration mode. The FTIR spectrum of CR after adsorption onto Cu₂O is much different from that before adsorption. Most of the absorption peaks disappear or weaken after adsorption onto Cu₂O (Fig. S3, curve b), indicating that the chemical bonds and the molecular structure of CR are destroyed after adsorption onto Cu₂O NPs [58]. These results imply that the adsorption of CR onto Cu₂O NPs is held by chemical activation or chemisorption.

For truncated octahedral Cu₂O particles, the mainly exposed surfaces are {111} and {100} planes [23,27] as illustrated in Fig. 8a. For cuprite structured Cu₂O, each 'O' is surrounded by a tetrahedron of 'Cu', and each 'Cu' has two 'O' neighbors as illustrated by its unit cell model (Fig. 8b). Along the {100} plane direction, the periodicity can be defined as two layers (layer 1 and layer 2 as shown in Fig. 8c). Layer 1 is composed by 'O' while layer 2 is dominated by 'Cu' atoms only. With respect to {111} plane direction, three atom layers consist of one period, while the 'Cu' layer is sandwiched between two layers of 'O' atoms (Fig. 8d). The distance between the two adjacent layers in such a period is so short that the three layers can be approximately regarded as in the same surface. Every two 'Cu' atoms has a dangling bond perpendicular to the {111} planes [27]. The surface 'Cu' atoms with dangling bonds on the {111} planes can make them being positively charged, and {111} planes can interact with negatively charged molecules or ions [59]. Therefore, anionic CR molecules may electrostatically interact with the $\{111\}$ planes of Cu₂O through the negatively charged sulfonic acid group (Fig. 9). Furthermore, theoretical study has shown that aniline can be adsorbed onto the $\{110\}$ and $\{111\}$ surfaces of Cu₂O by the interactions of the nitrogen lone pair electrons with Cu atom and the hydrogen atom of the amine group of aniline with the O atom of Cu_2O [60]. So, it is rational to deduce that CR may bind to Cu₂O through the interactions between the amine group of CR and the $\{100\}$ and $\{111\}$ surfaces of Cu₂O as illustrated in Fig. 9, which is similar to the interaction of aniline with Cu₂O. Based on the above results and discussion, it is possible



Fig. 10. (a) Schematic illustration of the experimental procedure of adsorption and regeneration of the Cu₂O adsorbent. (b) Cyclability of the as-prepared Cu₂O adsorbent.

that the interactions between the as-prepared Cu₂O NPs and CR are mainly dominated by chemisorption, probably by electrostatic interaction, hydrogen bond as well as coordination bond (Fig. 9). By coincidence, during the preparation of this work, Zhang and co-workers [61] has reported the adsorption behavior of Cu₂O sub-micro-octahedra toward CR and put forward that the interaction of CR with Cu₂O is not a simple physical adsorption.

3.7. Photocatalytic regeneration and reusability of the as-prepared Cu_2O NPs

Reusability of an adsorbent is considered as an important economical aspect to minimize the cost of material. Since Cu₂O is a semiconductor and can adsorb visible light (see Fig. 4), the regeneration of the Cu₂O adsorbent is realized by visible light irradiation. The experimental procedure for the photocatalytic regeneration and reusability of the as-prepared Cu₂O NPs is illustrated in Fig. 10a. First, 50 mg Cu₂O was dispersed in 50 mL 1000 mg L⁻¹ CR solution for adsorption. After adsorption equilibrium, the mixtures of Cu₂O and CR was treated by visible light irradiation ($\lambda \ge 420 \text{ nm}$ [62]) at room temperature until the CR solution became nearly colorless. Then the Cu₂O NPs were recycled and reused for further cycles of adsorption. Five adsorption cycles were performed for the same batch of Cu₂O NPs. It can be seen that the removal percentage of CR is not significantly changed within five cycles (Fig. 10b), suggesting that the as-prepared Cu₂O NPs can be photocatalytically regenerated and reused without loss of adsorption capability.

4. Conclusion

In summary, polyhedral Cu₂O NPs with rough surfaces were prepared by a facile sonochemical aqueous precipitate method. The adsorption behavior of CR onto the as-prepared Cu₂O NPs was systematically investigated, which was found to be spontaneous, endothermic and obey pseudo-second order rate equation. The adsorption isotherm can be fitted well to Freundlich model. The as-prepared Cu₂O NPs exhibit unprecedented adsorption capability for the removal of Congo red with a maximum adsorption capacity of 3904 mg g⁻¹ at 20 °C, which is the highest reported value so far. Together with the thermodynamics parameters, our results show that chemisorption plays the dominating role in the adsorption process. In addition, the Cu₂O NPs adsorbent can be photocatalytically regenerated, recycled and reused without loss of its adsorption capability. This study indicates that the as-prepared Cu₂O NPs can be used as an efficient and recyclable adsorbent for the removal of CR from aqueous solution. The present work may shed new light on the application of Cu₂O NPs in environmental protection.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2015.02. 048.

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