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INFLUENCE OF Ce^{3+} DOPING ON THE ALGAL INHIBITING PROPERTIES OF COPPER/SEPIOLITE NANOFIBERS

Algal inhibiting materials were synthesized by the co-impregnation method. Cerium was taken as an algal inhibiting agent with copper/sepiolite utilized as the carrier. The algal growth inhibition was assessed based on the form of presence and distribution of $Cu^{2+}$and Ce^{3+} ions on the surface of sepiolite using X-ray diffraction (XRD) and SEM analysis. The results indicate that at 5 wt. % Cu content, 0.8 wt. % Ce and after heat treatment at 400 °C, the materials exhibit the best algal inhibiting capacity of 83.11%.

1. INTRODUCTION

Algae are a kind of aquatic plant, they could multiply greatly in a suitable environment. The fast development of industry and increase of nitrogen and phosphorus content in wastewater have led to the eutrophication of water worldwide, which inevitably promote algal growth of in water bodies. Algae are known to proliferate and die at incredible speed, wherein newborn algae not only clog water pipes and heat exchange equipment, but also induce microbiological corrosion at the same time. The death of algae would pollute water body due to algal toxins, which would severely impact the safety of drinking water [1, 2]. Therefore, effective methods to control of algae growth are very important for the development of economic and ecological environment.

Common methods known to inhibit growth of algal include physical methods such as ultraviolet radiation, ultrasonic and electromagnetic. These methods are usually restricted due to the operational difficulties, high cost, and poor durability [3–6], while the chemical methods are usually carried out by addition of chemical agents to water

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streams, which are hard to control due to the variability in the load and are a source of secondary pollution as well. In the present study, copper/sepiolite composite doped with cerium was synthesized and its potential as a new kind of non-pollution and high efficient algal inhibiting material was evaluated.

2. EXPERIMENTAL

All the chemical reagents used in the present study were analytical grade: fibrous sepiolite used was selected from a mining area in Hebei Province, China. *Scenedesmus obliquus* was chosen as the study object for algae inhibition experiment [7–11]. It is a kind of nature unicellular algae with advantages such as fast growth, high photosynthetic efficiency, strong adaptability and asexual reproduction, which is usually used as research material. Organization for Economic Coperation and Development (OECD) has designed it as standard algal species for algal growth test. *Scenedesmus obliquus* was purchased from the Chinese Academy of Sciences, Institute of Aquatic Organisms, the original density of the solution was 9.50×10^6 cells/cm^3.

Preparation and characterization of the samples. The sepiolite samples were pretreated in 0.5 mol/dm^3 HCl for 1 h before drying at 120 °C for 12 h. Then they were immersed in solutions of Cu $(NO_3)_2$ of various concentrations using incipient-wetness impregnation method and dried at 80 °C in vacuum to obtain Cu loaded sepiolite, which was referred to as Cu/sep. The concentration of copper were 1–6 wt. %. The samples of Cu/sep were then immersed in te Ce $(NO_3)_3$ solution using incipient-wetness impregnation method in vacuum conditions. The resulting material was dried at 80 °C under vacuum to obtain a series of composite contained copper and cerium, which was referred as Cu-Ce/sep. The content of cerium was 0–1.0 wt. %.

The samples prepared were subject to SEM, EDS, XRD and thermal analysis. The SEM analysis was performed using XL30ESEM-TMP, Philips. The XRD analysis was performed using Bruker D8 Discover diffractometer in the Bragg–Brentano geometry, using CuK_α radiation with a wavelength of 1.5417 nm, while the thermal analysis was carried out using an SDA 449 F3, Netzsch thermal analyzer. The light adsorption capacity of the inoculum containing *Scenedesmus obliquus* was analyzed using 756MC UV/Vis spectrophotometer, Persee, China.

Algae inhibition experiment. The algae inhibition experiments were carried out under condition of fluorescent lighting at room temperature of 25 °C. 100 cm^3 of the algae solution was placed in a conical flask each time together with 0.2 g sample of sepiolite composite. The algae inhibition rate was tested every 4 days using UV/Vis spectrophotometer and calculated according to the equation given below. At the wavelength of 680 nm, the relative rate of the cell growth was characterized by the absorbance of the algae solution. The inhibition rate of algae growth can be calculated according to the following formula:

$$S = \frac{\lg N_{tck} - \lg N_t}{\lg N_{tck} - \lg N_{0ck}} \times 100\% \qquad (1)$$

where, N_{tck}, N_t are the densities of algal cells after *t* days for a blank control group, and the experimental one, respectively, N_{0ck} – the initial cell density of the blank control group.

The tested relationship between the absorbance and the algae density was as follows

$$Y = 974.761X - 11.484 \qquad (2)$$

where, *Y* is the algal cell density, cells/cm^3, *X* – absorbance. The calibration curve of algal cell density has not been shown in the present paper.

3. RESULTS AND DISCUSSION

Water in sepiolite is bound in three different forms: adsorbed water molecules in the pore channels, crystallization water coordinated with magnesium ions, and structural water connected with magnesium ions in the octahedra. It is gradually released upon increasing temperature during the calcination process.

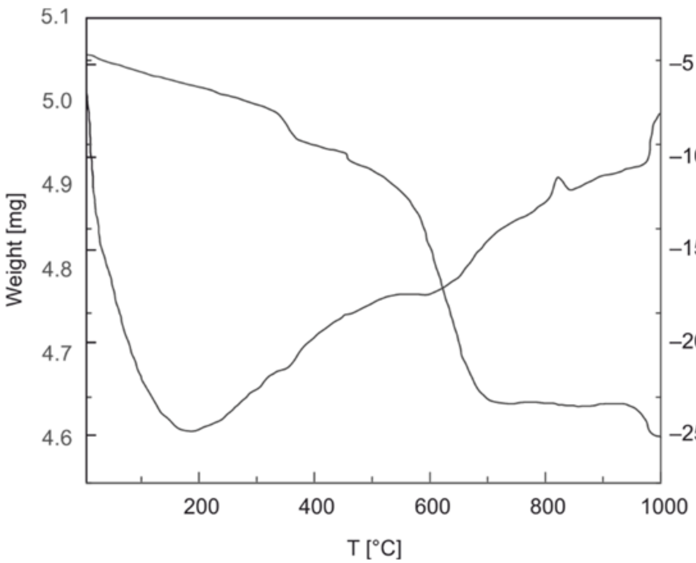

Fig. 1. Temperature vs. time for of Ce-Cu/sep sample

The results of thermal analysis of sepiolite are shown in Fig. 1. The three stages of water release are visible: the loss of adsorbed water, crystallization water and structural water at 200–400, 500–650, and 800–1000 °C, respectively. The exothermic peaks at 824 °C indicated a phase transformation of sepiolite after loss of crystallization water. Thus, in the present study, the temperature for thermal treatment of Cu/sep and Ce-Cu/sep samples was selected to be within the range of 250–450 °C.

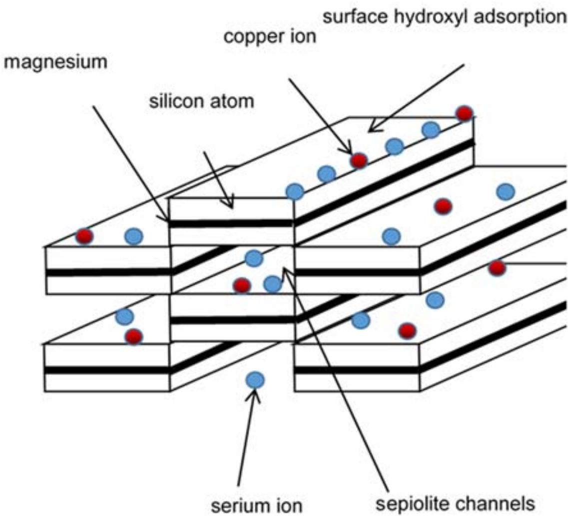

Fig. 2. Schematic of surface complexation adsorption

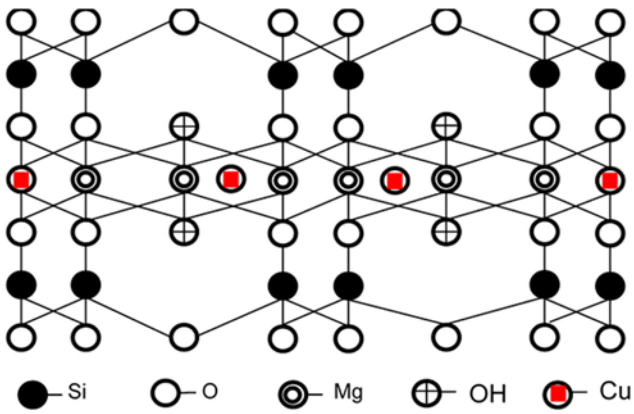

Fig. 3. Schematic of ion exchange adsorption

The acid treatment of sepiolite nanofibers could introduce more hydroxyl ions on the surface of sepiolite to form negative potential, thus, sepiolite fibers could adsorb metal ions in the solution. The Cu^{2+} and Ce^{3+} ions in the solution would migrate to form competitive adsorption due to electrostatic interaction. As a result, Ce^{3+} could form stable ions, in the center with hydroxyl group or water molecules as the ligand as shown in Fig. 2. It should be noted that Ce^{3+} ion could only be adsorbed on the surface of sepiolite fiber since its ion radius is about 0.115 nm, which is higher than that of Mg^{2+} in the skeleton of sepiolite fiber. The radius of Cu^{2+} ion is 0.072 nm, which is closer to the radius of Mg^{2+} ion (0.078 nm) in the fiber skeleton. Thus Cu^{2+} ions might replace Mg^{2+} ions to form a stable Cu–O structure. In addition, Cu^{2+} ions were also able to enter the vacant octahedral sites of magnesium ions as shown in Fig. 3. Since the rare earth element has a strong surface activity, adsorption of Ce^{3+} could increase the dispersion of Cu^{2+} on the fiber surface [12–14].

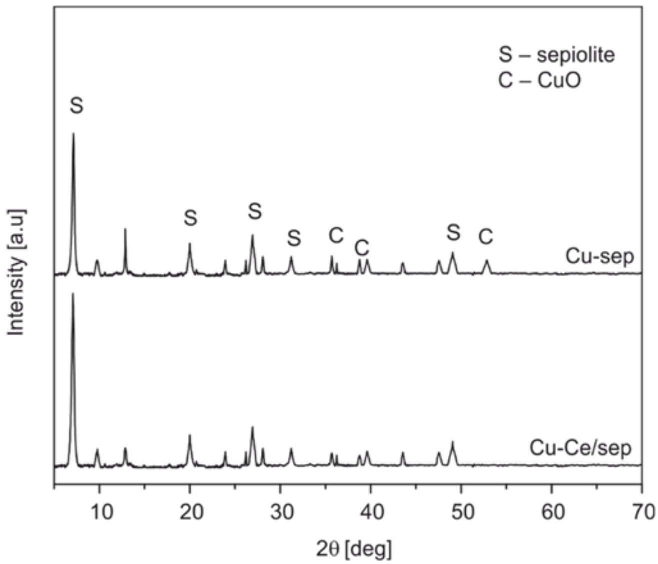

Fig. 4. XRD pattern of sepiolite composite

The XRD pattern of sepiolite nanofibers loading with Cu^{2+} and Ce^{3+} after the heat treatment is presented in Fig. 4. Characteristic diffraction peaks located at 35.5°, 38.7°, and 53° for Cu/sep and Ce-Cu/sep were assigned to CuO, corresponding to (002), (111), (020) crystal faces, respectively. It should be noted that there was no trace of cerium metal, or oxides observed in Fig. 4 for Cu-Ce/sep within the sensitivity of XRD. That may be due to the trace amount of cerium added in the sample. The characteristic peak intensity of CuO in Ce-Cu/sep is weaker, compared with Cu/sep this could be due to oxidization of Ce^{3+} into Ce^{4+} during the thermal treatment. The Ce^{4+} could only disperse on the surface of sepiolite nanofibers in the form of oxide (CeO_2) due to the large radius and higher chemical activity compared to Ce^{3+} [15], which finally influences the dispersion of CuO particles on the surface of sepiolite nanofibers.

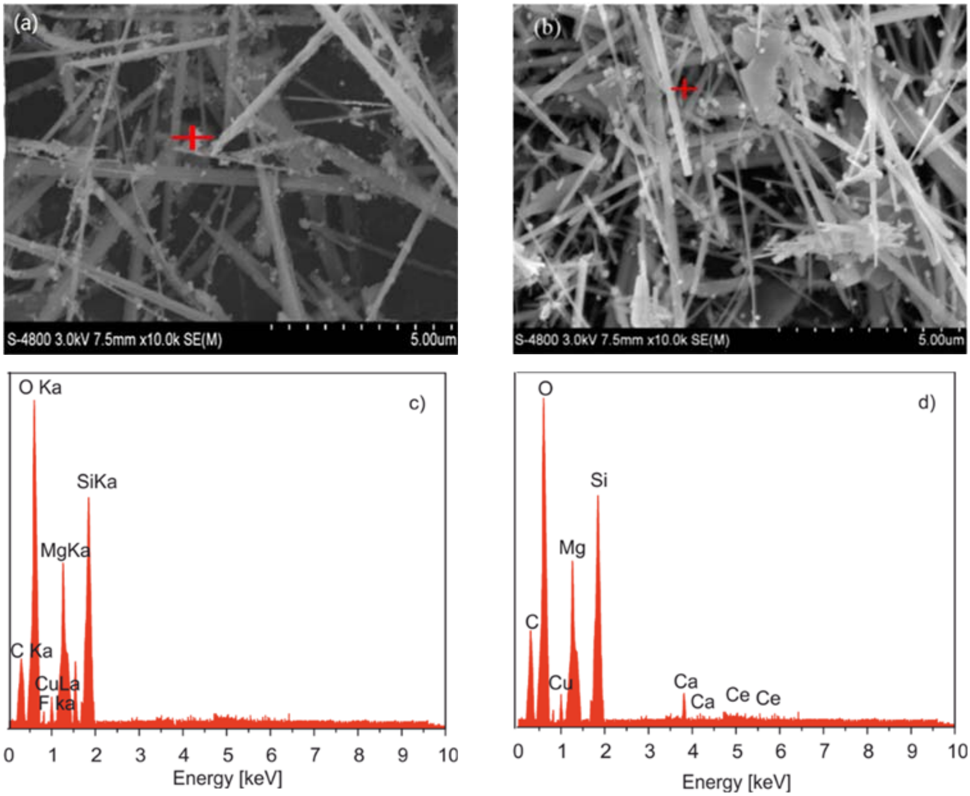

Fig. 5. Microstructure of sepiolite composite: a) SEM patterns of Cu/sep, b) SEM patterns of Ce-Cu/sep, c) EDS patterns of Cu/sep, d) EDS patterns of Ce-Cu/sep

The microstructure of sepiolite nanofibers loaded with Cu^{2+} and Ce^{3+} after heat treatment is shown in Fig. 5. A more uniform distribution of copper oxide could be observed after adding cerium (Fig. 5b). Additionally, the size of generated particles is much smaller in the range of 200–300 nm, which indicates Ce^{4+} being adsorbed on the surface of the sepiolite effectively inhibiting the growth of CuO grain to form more CuO particles, with better dispersity.

Figure 6 shows the growth inhibition rate of *Scenedesmus obliquus* at Cu loading in the range of 1–6 wt. %. An increase in the growth inhibition rate is observed upon increasing the incubation time for all concentrations of Cu loading. The inhibition rate increases gradually for 4 days, then it increases nearly exponentially to attain an asymptotic value after 12 days. The maximum growth inhibition rate is observed for copper content of 5 wt. %. This could probably be attributed to the dispersion and distribution of Cu in the sepiolite. At concentrations in excess of 5%, the particles could possibly reunite with each other, contributing to the reduction in the availability of Cu. Similar trend was also reported by Li [16] and Chen [17].

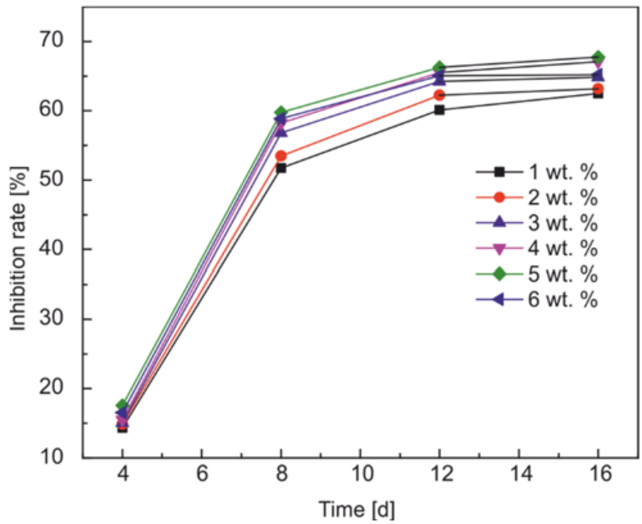

Fig. 6. Effect of Cu content on the inhibition rate at 25 °C

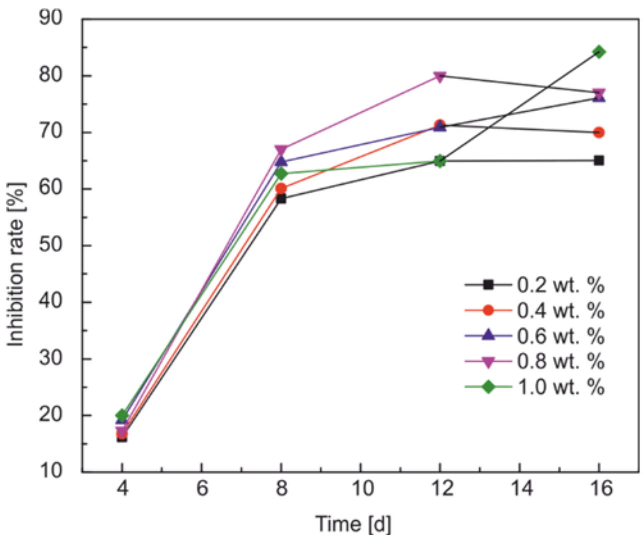

Fig. 7. Effect of Ce content on the inhibition rate at 25 °C (Cu content 5 wt. %)

The effect of different Ce doping (0.2–1 wt. %) on antialgal performance of the copper/sepiolite composite (copper content 5 wt. %) is shown in Fig. 7. The growth inhibition rate follows similar trend as reported in the previous section, however with the maximum inhibition rate of 83.11% at the Ce content of 0.8%. Any further increase in the Ce content was found to reduce the inhibition rate, which could be attributed to the competitive adsorption between Cu and Ce on sepiolite, which would affect the dispersion of Cu, further result in reunion of copper to generate larger particles in the heat treatment process. Jing et al. [18] and Li et al. [19] also reported reduction in algae inhibiting rate at high concentrations of cerium.

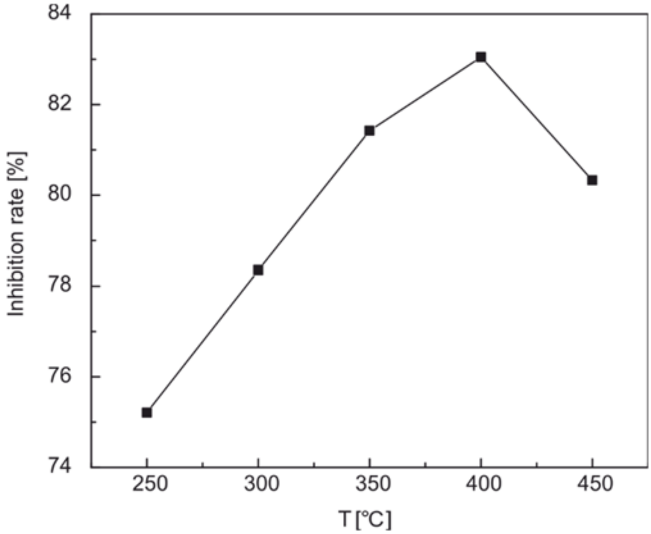

Fig. 8. Effect of heat treatment temperature on the inhibition rate at 25 °C
(Cu content 5 wt. %, Ce content 0.8 wt. %)

Ce-Cu/sepiolite materials prepared at various thermal treatment temperatures in the range of 250–450 °C were used to assess the antialgal performance. The inhibition rate of the composite increases upon increasing the thermal treatment temperature to a maximum of 400 °C (Fig. 8). The hydroxyl (–OH) ions in the sepiolite are mainly responsible for the adsorption of Cu^{2+} ions [20]. Upon increasing in the heat treatment temperature, the sepiolite structure along with the hydroxyl (–OH) is destroyed, resulting in reduced adsorption of Cu^{2+}.

In order to evaluate the persistence of antialgal performance of Ce-Cu/sep composite, two 100 cm^3 samples of water containing *Scenedesmus obliquus* were used. 0.2 g of Ce-Cu/sep was added to one sample, while the other acted as a blank one. After 30 days, the absorbances were measured (Fig. 9). For the blank sample, the absorbance increased rapidly in the first 16 days, to reduce its increase to the end of the experiment after 30 days, while the absorbance of the experimental sample did not change. It seems that the antialgal material has a long time influence on the growth of *Scenedesmus oblique*. The photographs of both samples are shown in Fig. 10. The color of the blank group turned darker upon time, while the experimental group treated by the Ce-Cu/sep composite looked transparent, which indicates the disappearance of the algae. This confirmed the effectiveness of antialgal activity of the Ce-Cu/sep composite.

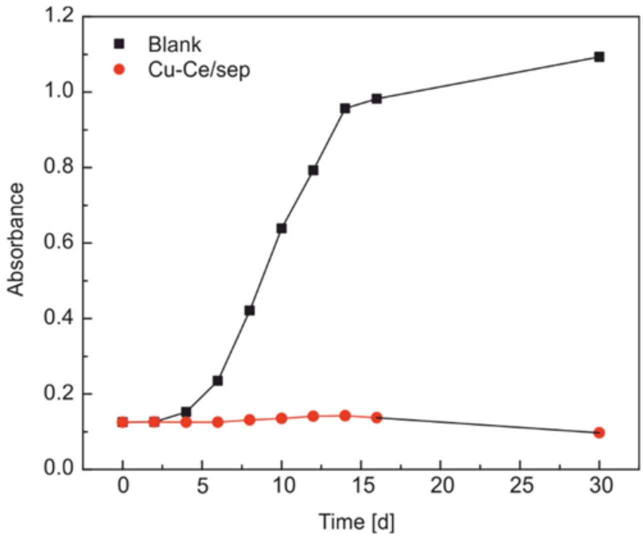

Fig. 9. Time dependences of absorbance at 680 nm of algal liquid
(Cu content 5 wt. %, Ce content of 0.8 wt. %, 25 °C)

Fig. 10, External appearances of algal samples after 30 days
(left – experimental sample, right – blank sample)

Cu^{2+} ions not only replace Mg^{2+} ions located in the sepiolite fiber skeleton, but also enter the octahedral sites, so that Cu^{2+} could be released into the solution slowly. When negatively charged algal cells are adsorbed onto sepiolite fibers, Cu^{2+} could diffuse into the algal cells and inhibit the growth of algae by influencing the photosynthesis.

After heat treatment, metal ions adsorbed on sepiolite fibers turned into copper oxide and cerium oxide nanoparticles with particle size about 200–300 nm and their distribution was homogeneous. At high nanoparticle concentration, one or more of antioxidant enzymes in algal cells would be stimulated displaying the phenomenon of "hormesis" to generate the effect of oxidative stress [21]. The cell metabolism could be destructed to influence the growth of algae. In addition, nanoparticles of metallic oxide would interfere the energy conversion, thus affecting the synthesis of ATP and have a blocking effect on cell cycle [22].

4. CONCLUSION

Sepiolite based antialgal material Ce-Cu/sep has been synthesized with Cu^{2+} ions in the sepiolite skeleton structure while the Ce^{3+} ions mostly attached on the surface and in the pore structure of sepiolite fibers. Addition of Ce^{3+} ions to Cu/sep contributed to the increase in the dispersion of Cu^{2+}. At the Cu loading of 5 wt. %, with Ce doping at 0.8 wt. %, heat treating at 400 °C, the inhibition rate was 83.11%. The effect of inhibition was effective for a month, confirming significant increase in the antialgal capacity of the Ce doped composite. The experimental results highlight the potential of Ce doped copper/sepiolite composite as an effective material for water treatment.

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