International Journal of Scientific Engineering and Applied Science (IJSEAS) – Volume-2, Issue-10,October 2016
ISSN: 2395-3470
www.ijseas.com

Preparation of carbon nanosphere/layered double hydroxide nanocomposites and their application for Cu(II) removal from water

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ABSTRACT:
Carbon nanosphere/layered double hydroxide (CN/LDH) nanocomposites were synthesized and used as an adsorbent for Cu^{2+} removal in wastewater. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology of the as-prepared materials. The optimum pH for Cu^{2+} removal was 5.0. The equilibrium data for the adsorption of Cu^{2+} onto CN/LDH could be described by the Langmuir isotherm model. Kinetics study showed that the adsorption process was well fitted by pseudo-second-order model. The maximum adsorption capacity was 38.16 mg/g.

Key words: adsorption, nanocomposite, Cu^{2+}

Introduction

Heavy metal contamination is a widespread environmental problem that poses serious threats to human health and ecosystem.[1] Copper ion is one of the common heavy metal ions, which is often used in the industries of mining, smelting, electroplating, brass manufacturing, etc. Copper is one of the elements necessary to maintain the normal growth, development and metabolism of a variety of biological life activities, however, the excessive intake of copper in human bodies accumulates in livers and produces gastrointestinal problems, kidney damage and anemia.[2] The permissible limit of copper discharge from industrial effluents into water bodies is limited to 0.25 mg/L.[3] Therefore, the effective treatment of copper ion attracts great attention. Nowadays, a large number of technologies have been used for Cu^{2+} treatment, such as liquid–liquid extraction[4], ion exchange[5], electrodialysis[6], biosorption[7], chemical precipitation[8]. Among which, adsorption is a promising method due to its simplicity and low cost.

Nanoparticles provide unprecedented opportunities for heavy metal ions removal in highly efficient and cost-effective ways.[9] Although remarkable achievements have been made for

anoadsorbents, the complexity of the process and the cumbersome of production hinder its commercial applications. Hence, it is urgent to design and manufacture high efficiency nanoadsorbents with simple fabrication process and low cost. Carbonaceous materials are common absorbents because of their rigid porous structures, high chemical and thermal stability. Xu and co-workers reported a new hierarchical carbon material and exhibited excellent adsorption capability for CrO_4^{2-} and Fe^{3+}.[12] Demir-Cakan and co-workers synthesized functional carbon particles by carbonization of glucose in the presence of acrylic acid monomer under hydrothermal treatment, and used them for Pb^{2+}, Cd^{2+} removal.[13] Layered double hydroxides (LDHs) have a large inner surface area and easily accept guest molecules, they are often used as adsorbents. He et al. reported that a hierarchical Mg-Al LDH framework on aluminum foam, which has highly selectivity and efficiency for Cr^{6+} adsorption.[14]

In this work, carbon nanospheres (CNs) were synthesized by a hydrothermal method, then mixed with Mg-Al LDH by sonification to form CN/LDH nanocomposites, their adsorption performance for Cu^{2+} were investigated.

Experimental Section

2.1 Materials and Apparatus.

$Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ were purchased from Tianjin Chemical Reagent Company. CH_3OH, NaOH, glucose ($C_6H_{12}O_6{\cdot}H_2O$) were obtained from National Medicines Corporation Ltd. of China, and all other chemicals were purchased from Sigma Aldrich with a purity higher than 99 %. Deionized water was used throughout the experiments.

2.2 Preparation of CNs, MgAl-LDHs and CN/LDHs.

CN was prepared through a typical method.[16] 17.6 g of glucose was dissolved in 120 mL of distilled water and transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained at 100 °C for 10 h, then cooled down to room temperature naturally. A dark precipitate was collected and further washed with absolute ethanol for several times. The obtained sample was then dried in a vacuum at 60 °C for 12 h.

2.3 Synthesis of MgAl-LDHs.

MgAl-LDH was synthesized according to a previously described method.[17] Typically, 30 mL of an aqueous solution containing 3.0 mM of $Mg(NO_3)_2{\cdot}6H_2O$ and 1.0 mM of $Al(NO_3)_3{\cdot}9H_2O$ were added into 120 mL of NaOH methanol solution (0.225 M) under vigorous stirring. Then the mixed solution was continuously stirred with nitrogen-bubbling for another 30 min and transferred into a Teflon-lined stainless steel autoclave. The autoclave was maintained at 150 °C for 18 h, then cooled down to room temperature. MgAl-LDH was collected and washed with absolute ethanol for three times and dispersed in water.

2.4 Direct Assembly of LDH on the Surface of CN.

0.4 g of LDH was dispersed in 20 mL of methanol, ultrasonicated till to disperse evenly, 0.1 g of CN was added to this methanol solution, then sonicated for 30 min. The CN/LDH nanocomposites were finally collected by centrifugation and dispersed in water.

2.5 Absorption

5 mg of CN/LDH was added to 5 mL water with different concentrations of Cu^{2+}, then shook at a speed of 300 rpm/min under room temperature for 18 h (ZHWY-103B thermostat shaker). The pH of aqueous solution was adjusted by 0.1M HCl or 0.1M NaOH solutions and measured by a pH meter (pHS-25). After adsorption equilibration, the adsorbents were separated by a centrifugation and the supernatant was analyzed by flame/graphite furnace atomic absorption spectrophotometer (AA-7000). For the kinetic study, the CN/LDH was kept at 1.0 g/L, and the concentration of Cu^{2+} was 50 mg/L. The adsorption amount Q was calculated according to the difference of Cu^{2+} concentration in the aqueous solution before and after adsorption, and the formula is as follows: [18]

$$Q = \frac{(C_0 - C_e) \times V}{W}$$

Where C_0 is the original concentration of metal cations; V is the total volume of solution, W is the dry weight of the hydrogel beads; C_e is the equilibrium concentration in solution.

2.6 Characterizations.

The morphology of CN, Mg Al-LDH, CN/LDH were characterized by Hitachi S-2500 scanning electron microcopy (SEM) and JEOL JEM-2010 transmission electron microscopy (TEM).

3. Results and discussion

3.1 Characterization of CN/LDH.

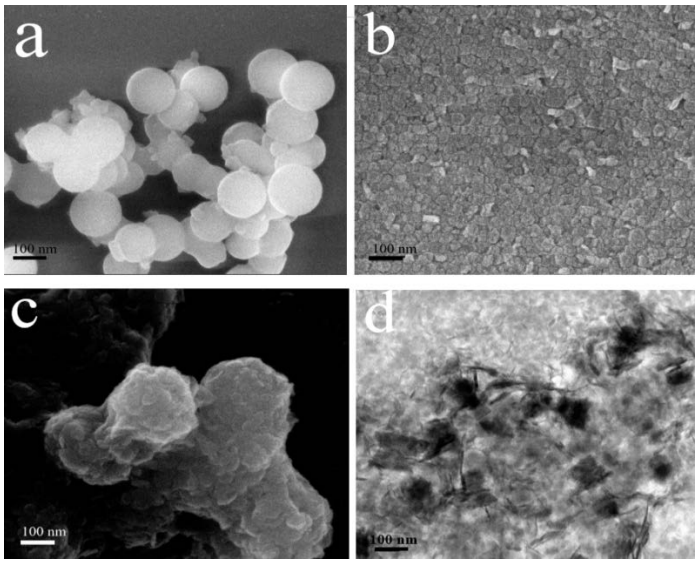

Fig.1 SEM images of CN (a), LDH (b), and CN/LDH (c), (d) TEM image of CN/LDH.

The CN are spherical nanoparticles with the size of 300-400 nm, as shown in Fig. 1a. Fig. 1b shows the LDH is lamellar structure and the size is 30-50 nm. After mixing CN with LDH, CN/LDH composites show rough surface (Fig. 1c), which proves LDH were successfully anchored on the surface of CN, this can be clearly observed in the TEM image (Fig. 1d).

3.2 The Effect of pH

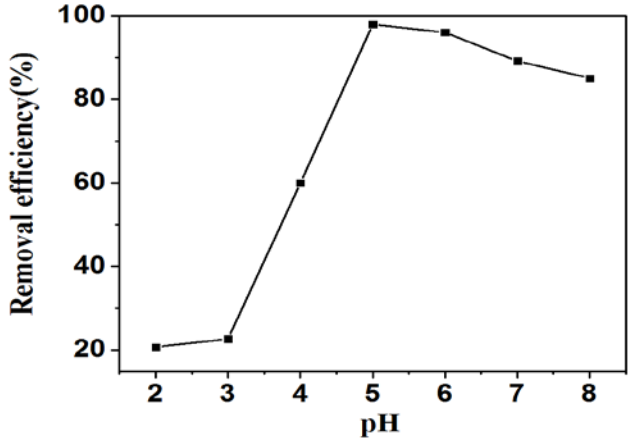

Fig. 2 Effect of pH on the removal of Cu^{2+} by CN/LDH (initial concentration of Cu^{2+} is 20 mg/L, adsorbent loading is 1 mg/mL, reaction time is 10 h, reaction temperature is 25°C).

The pH value plays an important role on the effective absorption.[19] Here, the removal efficiency of CN/LDH to Cu^{2+} in the range of 2.0-8.0 was investigated, the results are shown in Fig. 2. It can be seen that the removal efficiency of CN/LDH to Cu^{2+} increases with the increase of pH value from 2.0 (20.8%) to 5.0 (97.95%), this is due to large amount of H^+ ions compete for the adsorption sites in acid solution,[20] resulting in low removal efficiency. The absorption efficiency decreased to 84.0% as pH value increase to 8.0, this is because hydrolysis of Cu (II) occured, forming $Cu(OH)^+$ and $Cu(OH)_2$, resulting in the decrease of removal efficiency.[21] Therefore, pH=5.0 was chosen as the optimum pH value.

3.3 Adsorption Isotherms.

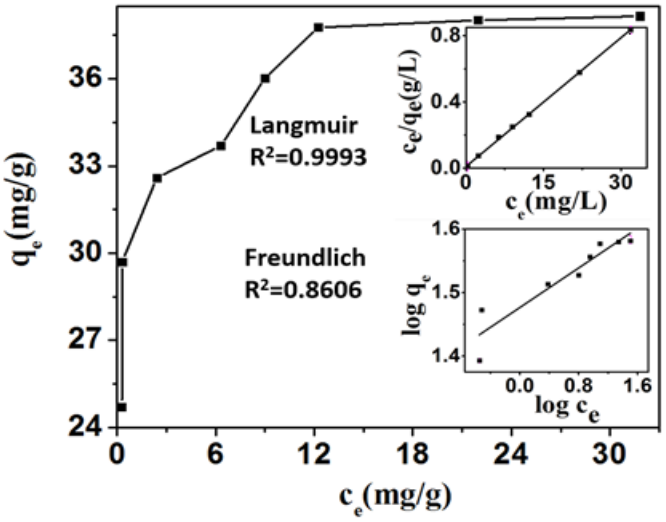

Fig. 3 Effect of concentration of Cu^{2+} on the removal by CN/LDH. Insets are the fitting results of the experimental adsorption isotherm data in terms of Langmuir and Freundlich models (pH is 5.0; reaction time is 10 h, adsorbent dose is 1 mg/mL, reaction temperature is 298 K).

Fig. 3 shows that the adsorption equilibrium isotherms for Cu^{2+} by CN/LDH. With the increase of the concentration of Cu^{2+}, the adsorption capacity increases. When the concentration of Cu^{2+} increased to 30 mg/g, the adsorption amount almost no longer increased, and the adsorption reached equilibrium. In the present study, Langmuir[22] and Freundlich[23] isotherms models were used to fit the adsorption data, they are expressed by eq (1) and (2).

Langmuir isotherm is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m}\frac{1}{C_e} \qquad (1)$$

The Freundlich adsorption isotherm can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (2)$$

Where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration in solution (mg/L), both at equilibrium. K_L (L/g) is the Langmuir constant and q_m (g/mg) is the maximum adsorption capacity of adsorbent. The Freundlich adsorption isotherm constants 1/n and K_F can respectively represent the adsorption intensity and capacity.

The parameters of Langmuir and Freundlich isotherm models for Cu^{2+} adsorption onto the CN/LDH are given in Table 1. The values of R^2 for the Langmuir isotherm and Freundlich model are R^2=0.9993 and R^2=0.8606, indicating that the equilibrium data for the adsorption of Cu^{2+} onto CN/LDH can be better described by the Langmuir isotherm model than Freundlich equation. Moreover, the calculated maximum adsorption capacity of Cu^{2+} of CN/LDH is 38.16 mg/g, which is higher than most of reported results.[24, 40]

Table 1 Adsorption isothermal parameters of Cu^{2+} on CN/LDH

	Langmuir adsorption isotherms			Freundlich adsorption isotherms	
	q_m (mg/g)	b (L/mg)	R^2	n	R^2
Cu^{2+}	38.16	0.602	0.9993		0.8606

3.4 Adsorption kinetics

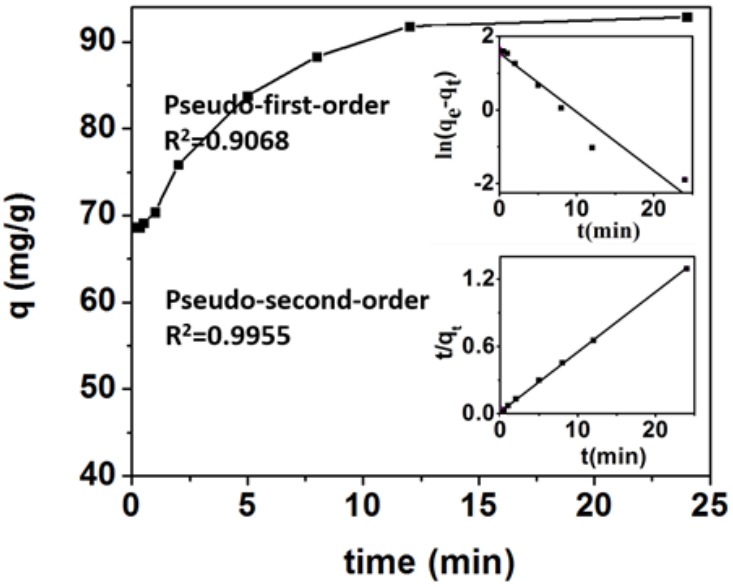

Fig. 4 Effect of reaction time on the removal of Cu^{2+} by CN/LDH . Insets are the fitting results of the experimental adsorption kinetic data in terms of pseudo-first-order and pseudo-second-order models. (initial concentration of Cu^{2+} is 50 mg/L, adsorbent dose is 1 mg/mL, reaction temperature is 25°C)

Table 2 **Adsorption kinetics parameters of Cu^{2+} on CN/LDH**

	Pseudo-first-order			Pseudo-second-order		
	q_e(mg/g)	K (h^{-1})	R^2	q_e(mg/g)	K_{ad}(g/(mg·h))	R^2
Cu^{2+}	46.42	0.213	0.9068	46.42	0.019	0.9955

Kinetics of adsorption was investigated by measuring adsorption capacity at different time, as shown in Fig 4. Pseudo-first order kinetic model (eq 3) and pseudo-second order kinetic model (eq 4) were used to identify the adsorption kinetics.[22]

The pseudo-first order equation is expressed as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

The pseudo-second order equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \qquad (4)$$

Where k_1 (min^{-1}) represents the adsorption rate constant， and k_2 (g/ (mg. min)) is the pseudo second-order rate constant, q_e (mg/g) and q_t (mg/g) represent Cu^{2+} adsorbed at equilibrium time and at time t. As shown in Table 2. The adsorption data can be better described by pseudo-second-order kinetic model. It means the adsorption capacity of CN/LDH was

proportional to the number of active sites on its surface.[25]

3.5 Adsorption mechanism

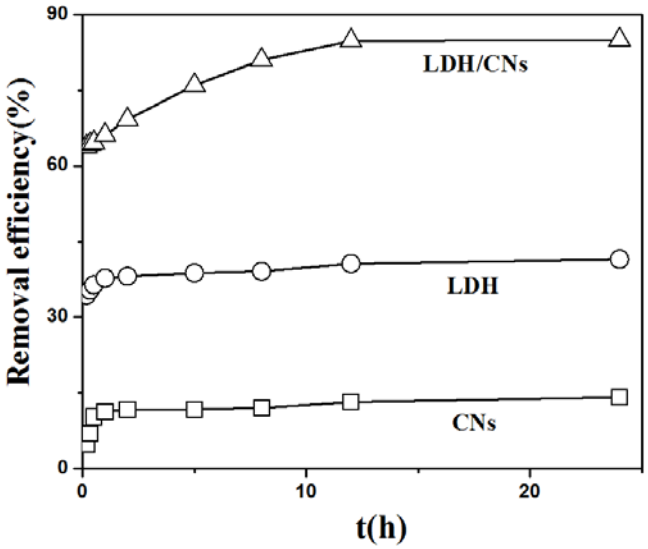

Fig. 5 Removal efficiency of different adsorbent on Cu^{2+} (initial concentration of Cu^{2+} is 50 mg/L, adsorbent dose is 1 mg/mL, reaction time is 10 h, reaction temperature is 25 °C).

In order to make a comparison, the removal efficiency of Cu^{2+} by using CN and LDH were investigated, as shown in Fig.5, it shows LDH plays a primary role on Cu^{2+} absorption, generally speaking, three aspects are usually thought as main reasons for heavy metal ions removal by LDH: (1) hydroxyl binding of heavy metal ions on the surface of LDH; (2) isomorphous substitution; (3) heavy metal ions deposited onto the surface of the adsorbent. The removal efficiency of CN and LDH are 13.08% and 40.67%, respectively. However, the removal efficiency of CN/LDH is 84.98%, which more than the sum of CN plus LDH, it implies there is a synergistic effect between LDH and CN, which can increase the removal efficiency.

4. Conclusion

In summary, we fabricated CN/LDH nanocomposites and investigated their adsorption performance for Cu^{2+} removal. The maximum adsorption capacity was 38.16 mg/g under optimized adsorption conditions. The adsorption kinetics were better consistent with a pseudo-second-order model (R^2 > 0.9955), and the equilibrium adsorption data was well described by the Langmuir isotherm model (R^2 > 0.9993). The results show CN/LDH nanocomposites have great potential in wastewater treatment, the application in real wastewater treatment will be included in our future work.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China 21501106, the Taishan Scholarship, the Shandong Province High Education Research and Development Program (J13LA08).

References

(1) Liang X, Zang Y, Xu Y, et al. Sorption of metal cations on layered double hydroxides [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013, 433: 122-131.
(2) Singha B, Das S K. Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes [J]. Colloids and Surfaces B: Biointerfaces, 2013, 107: 97-106.
(3) Zhu B, Fan T, Zhang D. Adsorption of copper ions from aqueous solution by citric acid modified soybean straw[J]. Journal of hazardous materials, 2008, 153(1): 300-308.
(4) Arous O, Gherrou A, Kerdjoudj H. Removal of Ag (l), Cu(II) and Zn(II) ions with a supported liquid membrane containing cryptands as carriers[J]. Desalination, 2004, 161(3): 295-303.
(5) da Fonseca M G, de Oliveira M M, Arakaki L N H, et al. Natural vermiculite as an exchanger support for heavy cations in aqueous solution[J]. Journal of Colloid and Interface Science, 2005, 285(1): 50-55.
(6) Öğütveren Ü B, Koparal S, Özel E. Electrodialysis for the removal of copper ions from wastewater [J]. Journal of Environmental Science & Health Part A, 1997, 32(3): 749-761.
(7) Hasan S H, Srivastava P. Batch and continuous biosorption of Cu 2+ by immobilized biomass of Arthrobacter sp [J]. Journal of environmental management, 2009, 90(11): 3313-3321.
(8) España J S, Pamo E L, Pastor E S, et al. The removal of dissolved metals by hydroxysulphate precipitates during oxidation and neutralization of acid mine waters, Iberian Pyrite Belt [J]. Aquatic Geochemistry, 2006, 12(3): 269-298.
(9) Xin X, Wei Q, Yang J, et al. Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe_3O_4 nanoparticles[J]. Chemical Engineering Journal, 2012, 184: 132-140.
(10) Li Y H, Wang S, Luan Z, et al. Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes [J]. Carbon, 2003, 41(5): 1057-1062.
(11) Strelko V, Malik D J. Characterization and metal sorptive properties of oxidized active carbon [J]. Journal of colloid and interface science, 2002, 250(1): 213-220.
(12) Xu Y J, Weinberg G, Liu X, et al. Nanoarchitecturing of activated carbon: facile strategy for chemical functionalization of the surface of activated carbon[J]. Advanced Functional Materials, 2008, 18(22): 3613-3619.
(13) Demir-Cakan R, Baccile N, Antonietti M, et al. Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid[J]. Chemistry of Materials, 2009, 21(3): 484-490.
(14) He S, Zhao Y, Wei M, et al. Fabrication of hierarchical layered double hydroxide framework on aluminum foam as a structured adsorbent for water treatment [J]. Industrial & Engineering Chemistry Research, 2011, 51(1): 285-291.
(15) Cavani, F.; Trifirb, F.; Vaccari, A. Hydrotalcite-type anionic clays: preparation, properties and applications. Catal. Today 1991, 11, 173–301.
(16) Sun, X. M.; Li, Y. D. Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles. Angew. Chem., Int. Ed. 2004, 43, 597–601.
(17) Gunawan, P.; Xu, R. Direct assembly of anisotropic layered double hydroxide (LDH) nanocrystals on spherical template for fabrication of drug-LDH hollow nanospheres. Chem.

Mater. 2009, 21, 781–783.
(18) Sui N, Wang L, Wu X, et al. Polyethylenimine modified magnetic graphene oxide nanocomposites for Cu $^{2+}$ removal[J]. RSC Advances, 2015, 5(1): 746-752.
(19) Ali I. New generation adsorbents for water treatment [J]. Chemical Reviews, 2012, 112(10): 5073-5091.
(20) Monier M, Ayad D M, Wei Y, et al. Adsorption of Cu (II), Co (II), and Ni (II) ions by modified magnetic chitosan chelating resin[J]. Journal of Hazardous Materials, 2010, 177(1): 962-970.
(21) Yuvaraja G, Subbaiah M V, Krishnaiah A. Caesalpinia bonducella leaf powder as biosorbent for Cu (II) Removal from aqueous environment: Kinetics and isotherms [J]. Industrial & Engineering Chemistry Research, 2012, 51(34): 11218-11225.
(22) Freundlich U. Die adsorption in lusungen[J]. 1906.
(23) Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum [J]. Journal of the American Chemical society, 1918, 40(9): 1361-1403.
(24) Gong J, Liu T, Wang X, et al. Efficient removal of heavy metal ions from aqueous systems with the assembly of anisotropic layered double hydroxide nanocrystals @ carbon nanosphere [J]. Environmental science & technology, 2011, 45(14): 6181-6187.
(25) Guo Y, Zhu Z, Qiu Y, et al. Adsorption of arsenate on Cu/Mg/Fe/La layered double hydroxide from aqueous solutions [J]. Journal of hazardous materials, 2012, 239: 279-288.
(40) Hao Y M, Man C, Hu Z B. Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles [J]. Journal of Hazardous Materials, 2010, 184(1): 392-399.