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Removal of Methyl Orange from Aqueous Solution by Calcium Alginate/Multi-walled Carbon Nanotubes Composite Fibers

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Abstract

Adsorbent of calcium alginate/multi-walled carbon nanotubes (CA/MWCNTs) composite fiber was prepared by wet spinning. Adsorptions of methyl orange (MO) anionic dyes onto CA/MWCNTs composite fiber were investigated with respect to MWCNTs content, initial dye concentration and pH values. Results illustrated that introduction of MWCNTs could obviously increase the adsorption capacity (q_e) of MO onto CA/MWCNTs composite fibers. The equilibrium adsorption data were analyzed using two widely applied isotherms: Langmuir and Freundlich. The results showed that Langmuir isotherm fitted the experimental results well.

Key words: Calcium alginate; Multi-walled carbon nanotubes; Composite fibers; Methyl orange; Adsorption

1. Introduction

Dyes are extensively used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals and food industries, resulting in a steadily growing demand and production [1].With the increasing use of dyes, pollution from dye wastewater is becoming a serious environmental problem. Therefore, color

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removal from wastewater is very important for solving the ecological, biological and industrial problems associated with the dyes [2]. A number of promising techniques have been established for elimination of heavy metals and dyes from contaminated waters. Adsorption appears to offer the best advantages, although the chemical degradation and the biodegradation approaches also find applications.

Adsorption is a well-known equilibrium separation process, in which the adsorbent may be of mineral, organic or biological origin. Alginate, extracted mainly from brown seaweeds which is abundant in all the sea areas of the world, is one of the more effective biological adsorbents for several heavy metal ions [3]. However, the adsorption capacities of alginate for some dyes are barely satisfactory. On the other hand, multi-walled carbon nanotubes (MWCNTs) have large specific surface areas and have found utility as adsorbents for both aqueous organic and inorganic contaminants [4,5]. However, widespread usage of MWCNTs will cause increasing emissions to the water environment and result in human contact risk to MWCNTs.

In this work, CA/MWCNTs composite fiber was prepared using $CaCl_2$ as crosslinking agent by wet spinning. The composite fiber not only make full use of the good heavy metals and dyes adsorption properties of alginate and MWCNTs, but also prevent MWCNTs from breaking off the composites to cause second micro-pollution to water. Such technique is also a practical approach to overcome the high cost difficulty encountered in the use of CNTs for environmental remediation. Here, the adsorption properties for methyl orange (MO) orgnic dyes on CA/MWCNTs composite fiber were investigated by using batch adsorption method.

2. Materials and methods

2.1. Materials

Sodium alginate (SA, 180 cP) was purchased from the Qingdao Mingyue Company (Qingdao, China) Multi-walled carbon nanotubes (MWCNTs) with outer diameter 20nm and length 5–15 μm were purchased from Shenzhen Bill Science and Technology Corporation (Shenzhen, China). Methyl orange (MO) was purchased from Tianjin BASF Chemical Co. Ltd. (Tianjin, China). Calcium chloride ($CaCl_2$) was supplied by Shanghai Chemical Reagent.

2.2. Preparation of CA/MWCNTs composite fibers

Briefly, SA was dissolved in distilled water to produce a viscous solution with the concentration of 3 wt % SA after mechanical agitation for 4h at ambient temperature. Then different amount of CNTs were added into SA solution under constant stirring for 30 min at room temperature and then ultrasonic 15 min to achieve homogeneous dispersion. Spinning dope was prepared for different concentrations of nanotube and SA, as shown in Table 1. A narrow jet of spinning solution was injected through a 0.5 mm diameter needle into a coagulation bath containing a 5 wt % aqueous solution of $CaCl_2$, and then collected on a spindle outside the bath which was rotated. The coagulated fibers were washed several times with deionized water and then dried in air under tension.

2.3. Adsorption experiments

Adsorption experiments were performed 250 mL glass pyramid bottle. The expected pH was obtained by adjustment with 1 M HCl or 1 M NaOH solution using a pH meter (PHS-3G, pH meter precision). Samples were taken at different time intervals to carry out the kinetic study. The suspensions containing different concentrations of MO solutions were shaken with a magnetic stirrer. All of the bottles were

placed in a water bath at 25±1℃ and shaken for 2 hours. Throughout the experiment, the concentration of dyes before and after adsorption was measured by Double-beam UV-Vis spectrophotometer.

The adsorption amount q_t (mg/g) was calculated using the following equation:

$$q_t = V(C_0 - C_t)/m \quad (1)$$

where C_0 and C_t were the concentrations of dye in the solution before and after adsorption period of time (mg/L), respectively, m (g) was the mass of adsorbent and V (L) was volume of the dye solution.

The removed quantity of dye by the fibers was calculated as follows:

$$q_e = V(C_0 - C_t)/m \quad (2)$$

where C_0 (mg/L) represents the initial dye concentration, C_e (mg/L) is the equilibrium concentration of dye remaining in the solution, m (g) is the weight of dry fibers, and V (L) is the volume of the aqueous solution.

Table 1. Composition of SA/MWCNTs composite fibers

Sample	SA conc. in dispersion (wt%)	MWCNTs conc. in dispersion (wt%)	MWCNTs conc. in solid fiber (wt%)
CA	3.0	0.0	0.0
CA/MWCNTs1	3.0	0.3	9.1
CA/MWCNTs2	3.0	0.6	16.7
CA/MWCNTs3	3.0	1.0	25.0

3. Results and discussion

3.1. Effect of MWCNTs dosage

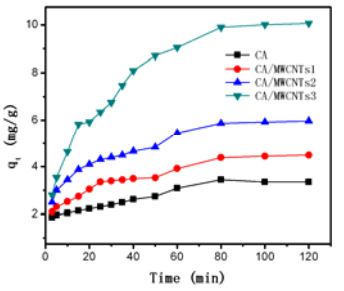

Fig. 1. Effect of MWCNTs content and contact time for the adsoption of MO onto fibers (C_0 = 100 mg/L, pH = 7.0).

The effects of MWCNTs content and contact time for the adsorption of MO onto CA/MWCNTs fibers were studied for a period of 2h for initial dye concentration of 100mg/L, as depicted in Fig. 1. It can be observed that the adsoption is initially (contact time < 45min) rapid, then slows. The reason can be explained that the initial fast adsorption was physical interaction of a surface. Then the slow adsorption was MO in water to the fiber internal migration, proliferation, the process was slow. From the Fig. 1, it can be found that the adsorption capacity was improved to a great extent with the MWCNTs content increased for CA/MWCNTs composite fibers. Results showed that introduction of MWCNTs could increase the adsorption capacity (q_e) of MO onto CA/MWCNT bioadsorbent with the MWCNT loading

increasing about 25.0% by 3 times as that of CA fiber. The low percent removal for CA fiber can be attributed to the fact that at pH=7.0, MO-type structure was azo negative charge, and the CA fiber surface may also bring a negative charge due to the deprotonation of carboxyl group. Under such conditions the MO do not adsorpt onto the CA fibers because of the electrostatic repulsion. Considering the above results, it could be concluded that the introduction of MWCNTs into CA fiber obviously increased the negative dye MO adsorption capability of CA.

3.2. Adsorption isotherms

The adsorption isotherms of MO on CA/MWCNTs fiber are shown in Fig. 2a. As can be seen from Fig. 2a, equilibrium uptake increased with the increasing of equilibrium dye concentrations at the range of experimental concentration. This is a result of the increase in the driving force from the concentration gradient. In the same conditions, if the concentration of dye in solution was higher, the active sites of CA/MWCNTs fibers were surrounded by much more dye ions, and the process of adsorption would carry out sufficient. Therefore, the values of q_e increased with the increase of equilibrium dye concentrations.

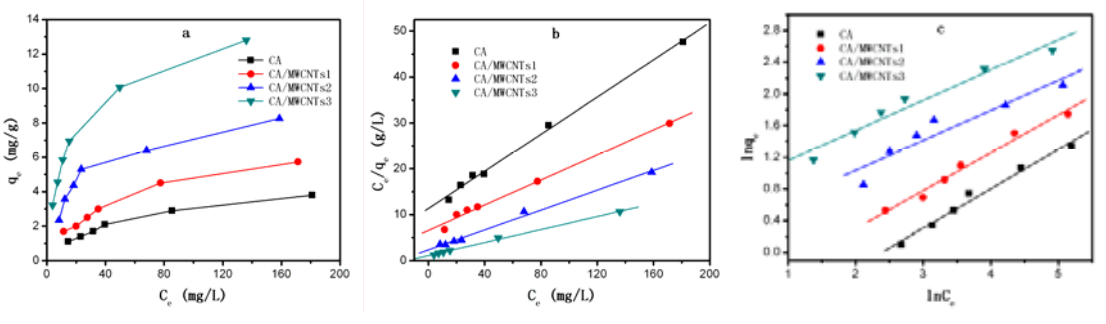

Fig. 2. Adsorption isotherms (a), Langmuir (b) and Freundlich (c) isotherms for MO dye adsorption onto CA and CA/MWCNTs fibers.

The adsorption data were analysed with the help of the following two important isotherms: the Langmuir and Freundlich isotherms. The linear form of the Langmuir equation [6] is

$$C_e/q_e = 1/(q_0 K_L) + C_e/q_0 \quad (3)$$

where C_e is the liquid-phase equilibrium concentration of dye (mg/g), q_e is the solid phase equilibrium concentration (mg/g), q_0 is the maximum amount of dye per unit weight of adsorbent for complete monolayer coverage (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg). When C_e/q_e was plotted against C_e, straight line with slop $1/q_0$ was obtained (Fig. 2b), indicating that the adsorption of MO on CA and CA/MWCNTs fiber follows the Langmuir isotherm. The Langmuir constants K_L and q_0 were calculated from this isotherm and their values are listed in Table 2.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation [7] is linearized as follows:

$$\ln q_e = (\ln C_e)/n + \ln K_F \quad (4)$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the dye (mg/L). K_F and n are Freundlich constants, K_F (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the adsorbent and n giving an indication of how favorable the adsorption process. It is generally stated that

values of n in the range 2-10 represent good, 1-2 moderately difficult, and less than 1 poor adsorption characteristics [6]. The studied materials are good adsorbents for MO ($n > 2$). The plot of $\ln q_e$ versus $\ln C_e$ (Fig. 2c) gives straight lines with slop $1/n$. Fig. 2c shows that the adsorption of MO also follows the Freundlich isotherm. Freundlich constants (K_F and n) were calculated and listed in Table 2.

Table 2. Parameters Langmuir and Freundlich adsorption isothermal models for MO onto CA, CA/MWCNTs1, CA/MWCNTs2 and CA/MWCNTs3.

Adsorbents	Langmuir			Frundlich		
	q_0	K_L	R^2	n	K_F	R^2
CA	4.94	0.0178	0.9962	2.01	0.30	0.9819
CA/MWCNTs1	7.31	0.0207	0.9915	2.09	0.52	0.9817
CA/MWCNTs2	9.26	0.0456	0.9934	2.64	1.32	0.8909
CA/MWCNTs3	14.13	0.0639	0.9980	2.63	2.18	0.9593

3.3. Effect of solution pH

Initial pH is one of the most important factors that affect the adsorption process. It affects not only the surface charge of the adsorbent, but also the ionization degree of the adsorbate. The experiments were carried out in pH range 2.0-12.0 and the results are illustrated in Fig. 3. From the Fig. 3, it was observed that MO adsorbed decreased when pH increased from 2.0 to 12.0. As mentioned above, one of the contributions of MWCNTs adsorption played a major role on the adsorption capacity on MO for the CA/MWCNTs composite fibers. It meant that the charge sign on the surface of CA/MWCNTs adsorbent should be negative in a wide pH range (i.e., 2.0-12.0). It was because that the surface of MWCNTs were wrapped by CA, with the pH increased, ionization of the –COOH surface groups can occur, leading to the surface of the CA/MWCNTs fibres becoming negatively charged. Excessive $-COO^-$ ions might compete with the dye anions and hence obvious reductions in dye uptake were observed. Therefore, adsorption of MO by CA/MWCNTs3 fibres is favoured at lower pH values.

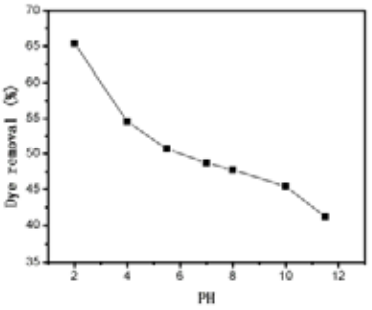

Fig. 3. Effect of pH for the adsoption of MO onto CA/MWCNTs3 fibers

4. Conclusions

Adsorbent of CA/MWCNTs composite fiber for effective MO removal has been prepared. The adsorbent towards MO has higher adsorption capacity due to the introduction of MWCNTs and the large specific area of fiber form of the composite. Batch adsorption experiments showed that the equilibrium

data was fitted with Langmuir isotherm equation. Based on Langmuir isotherm, the maximum equilibrium adsorption capacity of MO onto CA/MWCNTs3 can attain 14.13 mg/g. And the initial pH is one of the most important factors that affect the adsorption capacity of MO onto CA/MWCNTs composite fiber. The novel CA/MWCNTs composite fiber can be utilized as environment friendly adsorbent for the removal of MO from aqueous solution due to the efficient and fast adsorption process.

Acknowledgements

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