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Synergistic and competitive adsorption of cationic and anionic dyes on polymer modified yeast prepared at room temperature

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ABSTRACT

Poly (allylamine) modified yeast was prepared and used as an adsorbent for removal of cationic dye (rhodamine B) and anionic dye (congo red) from aqueous solution in single and binary dye systems. XPS and zeta potential analysis showed that the polymer was modified on the sorbent surface and isoelectric point of the sorbent increased from 3.2 to 9.5 after modification. Adsorption test showed that the amine groups modified yeast had higher adsorption capacity and affinity toward congo red than rhodamine B in single and binary system, revealing the electrostatic adsorption mechanism. In the single dye system, the adsorption capacities of the modified sorbent for congo red and rhodamine B were 0.24 and 0.03 mmol/g, respectively. In the binary system, rhodamine B adsorption was promoted by the presence of congo red (synergistic effect), but congo red adsorption was not promoted by the presence of rhodamine B. Antagonistic effect was observed for congo red adsorption at comparative high concentration of rhodamine B. It was for the first time to find that the ratio of the adsorption capacities for congo red and rhodamine B on the modified yeast was proportional to the ratio of the initial concentration of the two dyes. Total adsorption capacity of the modified yeast increased linearly both with the increase of the initial concentration of the two dyes.

1. Introduction

Organic dyes are excessively used in the textile, plastics, printing, and cosmetic industries [1,2]. The discharge of the colored wastewater is currently one of the world's major environmental problems because of their long-term environmental toxicity and short-term public health damage [3,4]. Although a number of processes are available for dye removal from aqueous systems, adsorption is the most convenient and popular method for its simplicity and high efficiency [5–10].

Due to the low cost and ready availability, more and more attention was paid on biosorbents, especially the waste biomass such as yeast and *Corynebacterium glutamicum* [11,12]. However, the native biomass had low adsorption capacity for cationic and anionic dyes. Since the adsorption of dyes mainly occurred on the sorbent surface, surface modification by functional groups would be an effective approach to enhance its adsorption capacity for dyes. Carboxyl and amine groups modified biosorbents have been prepared to improve its adsorption capacities for cationic and anionic dyes, respectively [13–17]. However, the adsorption performances of these modified biosorbents for dyes were mostly determined in one component system. For example, carboxyl groups modified biosorbents were applied to cationic dye adsorption, amine groups modified biosorbents were applied to anionic dye adsorption.

In fact, multiple components of cationic and anionic dyes are present in real wastewater systems simultaneously, and there may be interactions between different dyes during the adsorption process. Vijayaraghavan et al. [18] had investigated the effects of anionic dye: Reactive Red 4 (RR4), Reactive Orange 16 (RO16) and Basic Blue 3 (BB3) on the adsorption of anionic dye: Reactive Blue 4 (RB4) by immobilized *Corynebacterium glutamicum*, and found that the adsorption capacity of the sorbent for RB4 decreased from 184.5 mg/g to 126.9, 120.9 and 169.6 mg/g in the presence of RR4, RO16 and BB3. Turabik [19] had studied the competitive adsorption of cationic dye: Basic Red 46 and Basic Yellow 28 on bentonite, and obvious antagonistic effect were observed. Competitive adsorption of anionic dye: Reactive Orange 16 and Reactive Brilliant Blue R on polyaniline/bacterial extracellular polysaccharides composite were studied by Janaki et al. [20], and results showed that both the reactive dye anions compete with each other and resulted in lower uptake in the binary system. The above studies showed that there were mutual interactions between different dyes in the multi-component system on

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the unmodified sorbent. Compared with the multi-component dye adsorption on the unmodified sorbent, dye adsorption on the modified sorbent was more complex, and the competitive or synergistic effects of coexisting dye should be more significant. However, to our knowledge, dye adsorption on the modified biosorbents in the multi-component system had rarely been reported.

In this study, poly (allylamine) modified yeast were prepared at room temperature to improve its adsorption capacity for anionic dye. The adsorption performance of the modified yeast for cationic dye: congo red and anionic dye: rhodamine B was investigated in single and binary system. The mutual effects of the two dyes during the sorption process were studied in details. The relationship between the initial concentrations of the two dyes and the adsorption capacity of the sorbent were determined at the first time. Additionally, the adsorption mechanism was also discussed.

2. Materials and methods

2.1. Materials

Fleischmann's active dry yeast was purchased and washed with distilled water for 6 times. Then it was frozen dried before use. Poly (allylamine hydrochloride) (PAA) of average MW ~15,000 was purchased from AK Scientific, Inc. N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide (EDC), N-hydroxysuccinimide (NHS), $FeCl_2$ and $FeCl_3$ were purchased from Sigma Aldrich. All other chemical reagents were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemical reagents purchased were of analytical grade and used without further purification.

2.2. Preparation of the PAA modified yeast

A 1.18 g of NHS and 0.8 mL of EDC were added to 30 mL of distilled water containing 2.0 g of yeast. pH of the mixture was adjusted to 5.0 with HCl. After activation at room temperature for 40 min, 10 mL of PAA solution (10%, mass percentage) was added and pH was adjusted to 7.5 with NaOH. The yeast was collected by centrifugation after reaction at room temperature for overnight, and then it was washed with distilled water till neutral pH. The obtained modified yeast was then freeze dried and stored in a desiccator before use.

2.3. Characterization

XPS measurements were done on Axis 165 X-ray Photoelectron Spectrometer (Kratos Analytical) equipped with a monochromatic Al Kα X-ray source (hν = 1486.7 eV). All spectra were collected at room temperature with a base pressure of 1×10^{-9} Torr. CasaXPS software (version 2.3.16) was used for all data processing. Zeta potential measurements were performed on Nanosizer Nano (Malvern). Before test, the pH of the modified and unmodified yeast solutions were adjusted to designated pH. Average values of three replicates were used.

2.4. Batch adsorption experiment in one component system

Adsorption performances including isotherm and kinetics experiment were carried out at room temperature and 150 rpm on an orbital shaker. In the adsorption isotherms, 0.006 g of the modified or unmodified yeast was added into a 30 mL dye solution at natural solution pH (pH 5.8), and the initial concentrations of congo red(CR) and rhodamine B (RB) were ranged from 0.5 to 8.5×10^{-5} mol/L. In the adsorption kinetic experiment, 0.024 g of the modified yeast was added into 120 mL dye solution with the initial concentration of 4.0×10^{-5} mol/L for both dyes. The residual concentration of congo red and rhodamine B after adsorption was determined by measuring the absorbance at 498 nm and 554 nm, respectively. The adsorption capacity of the sorbent for dyes could be calculated by the following equation.

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where C_0 and C_e are the concentrations of the dyes before and after adsorption, respectively. m is the mass of the sorbent used and V is the volume of the dye concentration.

2.5. Batch adsorption experiment in the binary system

In this experiment, 0.006 g of modified yeast was added into 30 mL of the mixture solution of congo red and rhodamine B at pH 5.8. The initial concentrations of congo red used were 1.0×10^{-5}, 2.0×10^{-5}, 4.0×10^{-5}, 6.0×10^{-5} and 8.0×10^{-5} mol/L, respectively, and the initial concentrations of rhodamine B used were 0.5×10^{-5}, 1.1×10^{-5}, 2.1×10^{-5}, 4.3×10^{-5}, 6.4×10^{-5} and 8.5×10^{-5} mol/L at each initial concentration of congo red (shown in Table 1). After adsorption for 24 h, the supernatant was obtained by centrifugation. In order to subtract the mutual interference, the absorbance of each dye at their characteristic wavelength was calculated according to the following equations [18,20]:

$$A_{498}^{\text{Total}} = A_{498}^{\text{CR}} + A_{498}^{\text{RB}} \quad (1)$$

$$A_{554}^{\text{Total}} = A_{554}^{\text{CR}} + A_{554}^{\text{RB}} \quad (2)$$

$$\frac{A_{554}^{\text{CR}}}{A_{498}^{\text{CR}}} = \frac{\varepsilon_{554}^{\text{CR}} bC}{\varepsilon_{498}^{\text{CR}} bC} = \frac{\varepsilon_{554}^{\text{CR}}}{\varepsilon_{498}^{\text{CR}}} = K_1 \quad (3)$$

$$\frac{A_{498}^{\text{RB}}}{A_{554}^{\text{RB}}} = \frac{\varepsilon_{498}^{\text{RB}} bC'}{\varepsilon_{554}^{\text{RB}} bC'} = \frac{\varepsilon_{498}^{\text{RB}}}{\varepsilon_{554}^{\text{RB}}} = K_2 \quad (4)$$

$$A_{498}^{\text{CR}} = \frac{A_{498}^{\text{Total}} - K_2 A_{554}^{\text{Total}}}{1 - K_1 K_2} \quad (5)$$

$$A_{554}^{\text{RB}} = \frac{A_{554}^{\text{Total}} - K_1 A_{498}^{\text{Total}}}{1 - K_1 K_2} \quad (6)$$

where A_{498}^{Total} and A_{554}^{Total} are the total absorbance of the mixture solution at 498 and 554 nm, respectively. A_{554}^{CR}, A_{554}^{RB}, A_{498}^{CR} and A_{498}^{RB} are the absorbance of rhodamine B and congo red at 498 and 554 nm. $\varepsilon_{554}^{\text{CR}}$, $\varepsilon_{554}^{\text{RB}}$, $\varepsilon_{498}^{\text{CR}}$ and $\varepsilon_{498}^{\text{RB}}$ are the molar absorption coefficient of the dye at different wavelength, and K_1 and K_2 are the ratios of the molar absorption coefficient. C and C' are the concentrations of congo red and rhodamine B, respectively. The equilibrium concentration of congo red and rhodamine B were calculated according to the values of A_{498}^{CR} and A_{554}^{RB} by using the standard curve method.

3. Results and discussion

3.1. Characterization

Poly (allylamine) modified biomass was prepared by two steps [21,22]. Firstly, NHS and EDC were added to activate the carboxyl groups on the yeast surface at pH 5.0, and then EDC was substituted by the addition of the polymer at pH 7.5. Both of the reactions occurred at room temperature. Synthetic route to poly (allylamine) modified biomass was shown in Fig. 1. The inset of Fig. 2 shows the microphotograph (1000×) of the modified yeast, and it was found that the morphology of the yeast nearly did not change and it remained intact. Typical wide-scan spectra showed that the atomic ratios (calculated from the peak area) of C/N/O were 67.9:1.4:30.7 for the unmodified biomass, while those for the modified biomass were 70.3:3.8:20.9. The content of nitrogen increased significantly after modification. Fig. 2 shows the N1s spectra of the modified and unmodified yeast. One peak at 398.3 was observed in the spectrum of the unmodified yeast. Two new peaks at 397.9 and 400.1 eV, assigned