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Adsorption of Congo red from solution using cationic surfactant modified wheat straw in column model

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ABSTRACT

An agricultural by-product, wheat straw (NWS), was soaked in 1% a cationic surfactant (hexadecyl trimethyl ammonium bromide, CTAB) solution for 24 h (at 293 K) and modified wheat straw (MWS) was obtained. Then MWS was used as adsorbent for the removal of Congo red (CR, anionic dye) from aqueous solution. The experiment was performed in column mode at room temperature (293 K) and effects of initial CR concentration, flow rate, bed depth and common salt existed in solution on breakthrough curves were presented. The breakthrough curves became flatly at lower flow rate, lower CR concentration and higher bed depth and these conditions were advantageous of CR removal from solution. There is no significant effect of CR adsorption capacity at 0.1 mol/L sodium chloride solution. Thomas model and modified dose–response model were used to fit the column data using nonlinear analysis method and the fitted results were presented. Modified dose–response model was better to predict the breakthrough curves. 0.1 mol/L sodium hydroxide solution can elute CR adsorbed on MWS in column. The results implied that MWS can be selected as an inexpensive, effective and environmentally friendly adsorbent to remove CR from aqueous solution.

Introduction

Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents and it is proved to be an effective and attractive process for removal of refractory pollutants (including dyes, heavy metal ions, etc.) from wastewater [1,2]. Use of activated carbon as adsorbent has been found to be effective, but it is too expensive and the spent activated carbon can be regenerated with some mass lost. Thus, there is a demand for other adsorbents, such as inexpensive material from agricultural byproducts and industry waste with simple pretreatment step [3]. So the adsorption process will become economically acceptable. Many agricultural by-products, such as low-cost coconut-husk (for quinoline yellow) [4], rice husk (for anionic dye, Direct Red-31 and Direct Orange-26) [5,6], De-oiled Soya (for Eosin Yellow) [7], wheat straw (WS) (for methylene blue) [8,9], peanut husk (for methylene blue and neutral red) [10,11], beech sawdust (for methylene blue) [12], and tree leaves (for methylene blue) [13], were selected as adsorbents to remove dyes from solution.

However, the direct application of untreated agricultural by-products or waste as adsorbents can also bring several problems, such as lower adsorption capacity for anionic pollutants (as characteristic of the adsorbent with positive charge on surface), the release of soluble organic compounds contained in the raw materials (resulted in secondary pollution) [14]. Therefore it is necessary that these materials may be modified or treated before being applied for better application in adsorption [15,16].

Several researchers used cationic surfactant, such as hexadecyl trimethyl ammonium bromide (CTAB) and hexadecylpyridinium bromide (CPB) to modify agricultural byproduct to remove anionic ions or oil pollutants [17–19] and showed that adsorption quantity of modified materials toward pollutants was significantly improved. Wheat is widely planted in the north of China. So the yields of NWS from agriculture are vast, it represents a very low cost and is easily harvested. It is often used as a waste or feedstuff. Natural or modified wheat straw has been used as an available adsorbent to remove heavy metal ions and cationic dyes from water/wastewater [8,9]. The capacity about anionic dyes was very low. In our laboratory, CPB-modified wheat straw was prepared and the adsorption property toward light green (anionic dye) was presented in batch and column mode [19]. But the regeneration of dye-loaded adsorbent was not shown. Recently, CTAB modified wheat straw was used to remove methyl orange from solution in batch mode and regeneration was presented [20]. Through modification by cationic surfactant, adsorption capacity of wheat straw for anionic dye was markedly improved. In this paper, the surface of natural wheat straw (NWS) was modified using one cationic surfactant, hexadecyl trimethyl ammonium bromide (CTAB) in order to increase the adsorption capacity toward anionic

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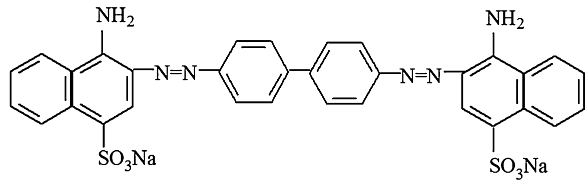

Fig. 1. Structure of Congo red.

dye from solution. Congo red dye (CR, C.I. 22,120, molecule weight 696.68 g/mol), a benzidine-based dye of the structure (see Fig. 1), was selected as objective. The dye is known to metabolize to benzidine, a known human carcinogen. Exposure to the dye has been known to cause an allergic reaction.

The adsorption capacity parameter obtained from the experiment in batch mode is useful in providing information about effectiveness of dye-adsorbent system. However, the data are generally not applicable to most treatment system (such as column operations). Hence, there is a need to perform dynamic studies using columns. The effects of flow rate and CR concentration on breakthrough curves were performed and regeneration of dye-adsorbents was performed. Thomas model and modified dose–response model were used to fit the column adsorption data and the fitted results were compared in order to obtain the better model to correlate the experimental data. Error analysis was carried out to test the adequacy and the accuracy of the model equations.

Thomas model

The expression of Thomas model for an adsorption column is given as follows [21]:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(A - Bt)} \tag{1}$$

where C_t is the effluent dye concentration at time t (mg/L), C_0 is the influent dye concentration (mg/L), A and B are constants from Thomas model. The value of C_t/C_0 is the ratio of effluent and influent CR concentrations. The value of t is flow time (min).

Modified dose–response model

The modified dose–response model [22] is also used to describe column adsorption data. Yan and his coworkers observed that use of this model minimizes the error resulting from the use of the Thomas model, especially at lower or higher time periods of the breakthrough curve. The expression is given as following:

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + (vt/b)^a} \tag{2}$$

where a and b are both parameters from modified dose–response model.

Error analysis

In this paper, a nonlinear regressive method was used. The statistic is basically the least sum of the squares of the differences between the experimental data and data obtained by calculating from models. So the values of *SS* (error) can be obtained as following formula:

$$SS = \sqrt{\frac{(y_c - y_e)^2}{n - 2}} \tag{3}$$

where $y = C_t/C_0$, y_c is the ratio of effluent and influent CR concentrations obtained from calculation according to dynamic models, and y_e is the ratio of effluent and influent CR concentrations obtained from experiment; n is the number of experimental points. In order to confirm the best fit isotherm for the column adsorption system, it is necessary to analyze the data using the values of *SS*, combined the values of R^2 [23].

Materials and methods

Preparation of adsorbent

The wheat straw used was collected from Zhengzhou countryside. The materials were washed with tap water several times to remove all the dirt particles and then washed with distilled water. The washed wheat straw was dried at 353 K for 24 h and cooled to room temperature. Then it was crushed and sieved to produce particles of 40–60 mesh. It was stored in a glass bottle and named as NWS. The NWS was treated as following procedures [17,20].

5.0 g of NWS and 200 mL solution (1% CTAB) were added to one 500 mL conical flask. Then the mixtures were shaken by an orbital shaker with 100 rpm (SHZ-82, Shanghai, China) at room temperature (293 K) for 24 h. Then the solid was separated from the mixtures and washed with distilled water several times for removal of superficially retained CTAB. Finally, it was dried at 333 K overnight (Electric heating oven, 202-V1, Shanghai, China) and MWS was obtained (stored in an airtight glass bottle).

The percentages of element are 0.226% N, 42.34% C, 5.81% H for NWS and 0.442% N, 46.32% C, 6.49% H for MWS, respectively [20]. The increased percentages of C, H and N were from CTAB adsorption, the content was calculated as 54.6 CTAB mg/g NWS from nitrogen content. The element Br was detected as 2.75% for MWS by X-ray fluorescence method while Br was not detected for NWS. TG analysis of NWS showed that solid residue is 8.5% when temperature is over 500 °C [16]. Comparison of FTIR between NWS and MWS, the vibration peak from $-CH_2$ of CTAB (at 2855 cm^{-1} and 1464 cm^{-1}) became stronger while the band at 3410 cm^{-1} (from $-NH_2$ and –OH) is broadened. These results showed that CTAB have adsorbed onto surface of NWS.

Preparation of CR solution

All reagents used in experiment were analytical-grade chemicals and were purchased from Zhengzhou Chemical Corporation in China. Stock solution (500 mg/L) was prepared by dissolving CR in distilled water. Working solutions were obtained by diluting the stock solution with distilled water to the desired concentration. Solution pH was adjusted to 5 from the results of effect of pH on CR adsorption.

Column adsorption studies

Continuous adsorption experiments in fixed-bed column were conducted in a glass column (1 cm ID and 25 cm height), packed with 0.53 g (6 cm), 0.72 g (9 cm), and 0.94 g MWS (12 cm), respectively. The effects of the following column parameters, on CR adsorption were investigated. (1) Effect of flow rate: flow rate was varied between 9, 12, 15 mL/min, while inlet CR concentration were held constant at 30 mg/L with 9 cm bed depth, respectively. (2) Effect of inlet CR concentration: inlet CR concentration was varied between 30, 50, 80 mg/L, at 9 mL/min flow rate and 9 cm bed depth. (3) Effect of bed depth: bed depth was varied between 6, 9, 12 cm with 10 mL/min flow rate and 30 mg/L CR. The effect of salt in solution was studied as following condition: 9 cm bed depth, 10 mL/min flow rate and 30 mg/L CR with 0.1 mol/L NaCl and $CaCl_2$, respectively. The experiments were conducted by pumping CR solution in down flow mode through the fixed-bed with a peristaltic pump (HL-4, Shanghai, China). The temperatures of all