Application of Cellulosic Biomass for Removal of Cationic Dye Rhodamine 6G from Aqueous Solutions

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Abstract

This study investigated the adsorption efficiency of treated newspaper pulp, Azollafiliculoides and date fibers as low-price and readily-available adsorbents for removal of the cationic dye Rhodamine 6G from aqueous solutions. The parameters influencing adsorption (aqueous phase pH, ionic strength, amount of adsorbent, adsorbent-water mixing time) were assessed and optimized. It was found that 0.3 g of each adsorbent removed 75%-95% of the dye (initial concentration 10 mg/L) from 45 mL of water at pH >2 after 30 min at 25°C. Treated newspaper pulp showed better adsorbent characteristics for removal of Rhodamine 6G than the other adsorbents. The kinetics of adsorption can be suitably described using a pseudo second-order model. The Langmuir, Temkin, Freundlich and Dubinin-Radushkevich models were tested to describe the equilibrium data of the adsorption. The Langmuir model successfully described the experimental data for the adsorption of Rhodamine 6G onto Azollafiliculoides.

Keywords: Azollafiliculoides; Date fiber; Cellulosic adsorbent; Newspaper pulp; Rhodamine 6G

Introduction

The textile, leather, rubber, paint, paper, plastic and cosmetic industries use a variety of chemicals in their production processes. They produce a significant amount of waste water containing toxic and harmful materials. Among these materials are pigments and dyes, which are known as the most dangerous substances [1]. Dyes adsorb and reflect sunlight entering water, diminishing photosynthesis of algae and seriously influencing the food chain. Because of their high thermal and light stability, dyes remain in the environment for a long time [2]. Rhodamine 6G (Figure 1) is a toxic dye used in silk, cotton, wool, baste fiber, paper, leather, and plastic production [3]. The toxicity and carcinogenic nature of this dye have been reported in detail by the US Department of Health and Human Services [4].

The physical, chemical and biological methods applied for removal of dyes from aqueous solutions include coagulation, flocculation, biological oxidation, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration and membrane processes [5]. The application of low-cost adsorbents is also of interest for this purpose [6]. Shale oil ash [7], sawdust [8], fly ash [9], Azollafiliculoides [10], palm ash [11], sunflower seed shells [12] and fungi are natural adsorbents used for the refinement of dyes in water samples [9]. The present study evaluates the abilities and properties of three low-cost cellulosic adsorbents for R6G removal from water solutions. The adsorbents are treated newspaper pulp (TNP), Azollafiliculoides (AZ) and date fiber (DF). The effect of aqueous solution pH and ionic strength, initial dye concentration, amount of adsorbent and contact time are investigated and discussed. The kinetics and adsorption isotherms of the process are also examined.

Materials and Methods

Rhodamine 6G (R6G), sodium bicarbonate, disodium hydrogen phosphate, hydrochloric acid and sodium hydroxide were of analytical reagent grade and were purchased from Merck. A stock solution of R6G (500 mg/L) was prepared using distilled water; working solutions were obtained by appropriate dilution of this stock solution. Spent newspapers were treated with sodium bicarbonate solution (5%) to remove grease, ink and bleaching materials. The resulting pulps were washed several times with distilled water, until the pH of the supernatant water layer was 6.5–7.0. A specific amount of pulp was refluxed with a solution of disodium hydrogen phosphate (5%) for 4 h. This impregnated the cellulosic matrix with phosphate ion. The pulp was then cooled and passed through filter paper (Whatman 40). The TNP was air-dried and was ground using a mixer grinder (Moulinex) to make it fluffy [13]. AZ was collected from the surface of Anzali lagoon in Guilan province (northern Iran). It was washed with distilled water three times to remove mud and then air-dried outdoors. The dried

Figure 1: The chemical structures of cationic dye Rhodamine 6G (R6G).

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AZ adsorbents were ground in a blender and sieved (63 μm mesh). Fresh date fiber (a raw living biomass) was collected from date palms (Phoenix dactylifera) from Yazd, the provincial center of Iran. It was washed with distilled water, cut into small pieces and dried outdoors for 3 d. It was then sieved (63 μm mesh) and stored without further chemical or physical treatment. The FT-IR spectra of the adsorbents were recorded on using a Nicolet iS10 FT-IR spectrometer. The stock solution (45 mL) (initial concentrations: 10, 30 and 50 mg/L) was introduced into a 100 mL round-bottomed flask at room temperature (25 ± 2°C). One of the sample adsorbents was added to the flask (0.3 g) and the mixture was stirred (250 rpm) for 30 min on a shaker (IKA KS 260). The solution pH was adjusted to 6.0 ± 0.5 by the addition of diluted (0.01 M) HCl or NaOH. Phase separation was performed by centrifuge (HeraeusLabofuge 300) at 2000 rpm. Analysis of the dye was carried out using a UV–Vis spectrophotometer (DR 5000) at the maximum wavelength of the dye (525 nm). The variation of the absorption of dye solution versus concentration was studied by using a series of standard solutions. The corresponding calibration curve was linear (R2=0.999) in the range 2-20 mg/L of dye's solutions. For this range the equation describing the variation of absorbance versus concentration was found to be as: Absorbance=(0.081×Concentration) - 0.002

The detection limit and relative standard deviation were 0.2 mg/L and 4.5%, respectively. The limit of quantification was 0.6 mg/L. The amount of dye adsorbed (qe, mg/g) was calculated using Equation (1)

\[ q_e = \frac{(C_0 - C_e)V}{M} \]

where \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of the R6G solution, respectively; \( V \) (L) is the volume of the solution; \( M \) (g) is the mass of the biosorbent; and \( q_e \) (mg/g) is the amount of dye adsorbed. All results are the means of experiments performed in triplicate.

**Results and Discussion**

Figure 2 shows the FT-IR spectra of the surface functional groups on the adsorbents. The spectra are summarized in Table 1. The presence of binding groups OH, NH, C=O and C=N and the possible π-π interaction of R6G with the adsorbent surface may be the mechanism of adsorption of the dye.

R6G is a cationic dye and ion pair formation is the main mechanism of adsorption, protonation and deprotonation of the functional groups on the surface of the adsorbents. This influences adsorption efficiency and suggests that efficiency depends on aqueous solution pH. A series of experiments was designed to investigate the effect of this parameter on removal efficiency. Each adsorbent (0.3 g) was added to 45 mL of aqueous solution containing different amounts of dye (10, 30 and 50 mg/L) and adjusted to produce a pH of 1 to 9. After 30 min of shaking, the mixture was filtered containing different amounts of dye (10, 30 and 50 mg/L) and adjusted to efficiency. Each adsorbent (0.3 g) was added to 45 mL of aqueous solution was designed to investigate the effect of this parameter on removal of the solution, Ms (g) is the mass of the biosorbent; and qe (mg/g) is the amount of adsorption of the dye.

The adsorption mechanism is described as follows: the dye binds to the functional groups on the adsorbent surface. This influences adsorption efficiency and suggests that efficiency depends on aqueous solution pH. A series of experiments was designed to investigate the effect of this parameter on removal efficiency. Each adsorbent (0.3 g) was added to 45 mL of aqueous solution containing different amounts of dye (10, 30 and 50 mg/L) and adjusted to produce a pH of 1 to 9. After 30 min of shaking, the mixture was filtered and the amount of dye remaining in the aqueous phase was determined spectrophotometrically. Figure 3 shows that adsorption efficiency increased as the pH of the solutions increased. This can be attributed to the negative charge on the surface of the adsorbents [14]. A schematic of the proposed mechanism for the adsorption of R6G molecules onto the surface of the cellulosic adsorbents is shown in Figure 4.

Maximum uptake of R6G (30 and 50 mg/L) occurred at pH>3 for TNP, pH>6 for AZ and pH>2 for DF adsorbents. At a pH>3, TNP and AZ adsorbed about 80% and DF adsorbed more than 70% of the dye (10 mg/L) was removed from the aqueous solutions. Based on these results, a pH of 6 was chosen for testing.

The uptake of R6G affects adsorption and was studied as a function of adsorbent dose (0.1-0.5 g). The solution pH was adjusted to 6 ± 0.2 and the initial concentrations of dye used were 10, 30 and 50 mg/L. Results showed that increasing the dose of adsorbent increased uptake efficiency (Figure 5). A comparison of the results reveals that efficiency varied as AZ > TNP > DF. This order of efficiency was confirmed by the data on the effect of pH. It was observed that removal efficiency decreased or remained nearly unchanged at values above 0.25 g for TNP and AZ and 0.30 g for DF. This can be attributed to the agglomeration of the adsorbent particles at higher doses [15].

Figure 6 shows that R6G removal increased as contact time increased. Maximum uptake of the dye was achieved after 20 min of shaking. The results show that relatively fast adsorption occurred during the first 20 min of shaking. AZ attained equilibrium after this time, but the other adsorbents showed a decrease in adsorption. The trend observed for AZ probably results from the availability of free surface sites for the first phase and the gradual occupancy of the active sites, decreasing the uptake percentage. The decrease in uptake after 20 min by TNP and DF can be explained by the slow kinetic desorption of the dye. The process probably occurs in a kinetically stable formation of ion-pairs for TNP and DF. A thermodynamically stable ion-pair can also be considered for the removal of R6G by AZ. The optimum time was found to be 20 min, at which point about 90% for TNP, 95% for AZ,
Figure 3: Effect of aqueous solution pH on R6G uptake by the studied adsorbents. Experimental conditions: 45 mL sample solution, 0.3 g of the adsorbent, shaking 250 rpm, temperature 25°C, contact time 30 min.

Figure 4: Proposed adsorption mechanism of R6G onto the surface of cellulosic adsorbent.

Table 1: Characterization of FT-IR spectra of adsorbents.

| Bond | v (Cm⁻¹) | Bond | v (Cm⁻¹) | Bond | v (Cm⁻¹) |
|------|----------|------|----------|------|----------|
| OH, NH | 3384 | OH, NH | 3416 | OH, NH | 3404 |
| CH of C₂ | 2920 | CH of C₂ | 2922 | CH of C₂ | 2919 |
| CO₂ | 1453 | CO₂ | 2399 | CO₂ | 2359 |
| C=O, OH | 1373 | CH₃ | 1637 | CH₃, OCH, CCH | 1434 |
| C=O, C=O | 1161 | C=O | 1617 | C=O | 1583 |
| C-OC, CC | 1000 | C-OC | 1384 | C-OC, OH, CCO | 1246 |
| C-C, CH, CCH | 3384 | C-O | 1025 | C-O | 1035 |

and 75% for DZ of the dye (10 mg/L) was removed from the aqueous phase.

The solution matrix can alter the efficiency of the adsorption process. To investigate this effect on the adsorption of R6G, its removal from an aqueous phase containing NaNO₃, KNO₃, CaCl₂, and NaCl (0.1-0.4 M) was verified (Figure 7). The decrease in the uptake of R6G is probably the result of adsorption competition between the cations of the salts and dye. A variation in the activity coefficients by salt concentration must also be considered.

Figure 6 plots dye uptake as a function of time. Simple Elovich, pseudo first-order, and pseudo second-order kinetics were applied to process the experimental data and examine the controlling mechanism of adsorption [16]. The simple Elovich model describes the kinetics of the chemisorption process as:

\[ q(t) = \frac{a q_e}{1 + b q_e t} \]

where \( q(t) \) is the amount of dye adsorbed at time \( t \) (mg/g), \( a \) is the rate of chemisorption at zero coverage (mg/g.min), and \( b \) is the desorption constant for the extent of surface coverage and activation energy for adsorption (K/mg). These parameters are both constant. The pseudo first-order kinetics can be expressed as:

\[ \log(q_e - q_t) = \log(q_e) - \frac{kt}{2.303} \]

where \( q_e \) is the amount of dye adsorbed at equilibrium (mg/g); \( q_t \) is the amount of dye adsorbed at time \( t \) (mg/g); and \( k \) is the pseudo first-order rate constant (1/min). The mathematical expression of the pseudo second-
order kinetic model is:
\[
\frac{t}{q_t} = k_2 q_e^2 + \frac{t}{q_e}
\]  
(4)

where \(k_2\) is the pseudo second-order rate constant (g/mg.min).

Table 2 shows the kinetic parameters for the kinetic. Note that the experimental data did not fit the pseudo-first-order model and, thus, the corresponding data is not shown. The pseudo-second-order model provided an impressive and comparable correlation for the adsorption of R6G dye over the other two models.

Adsorption isotherms describe how solutes interact with adsorbents and are used to design adsorption systems for practical or technological use. They are also useful for describing adsorption capacity to evaluate the feasibility of an appropriate adsorbent and for preliminary determination of the optimum amount of adsorbent. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were tested to describe the adsorption isotherms. The Langmuir model assumes that dye uptake occurs on a homogeneous surface by monolayer adsorption with no interaction with the adsorbed dye. The Freundlich model assumes that the uptake of dye occurs on a heterogeneous surface by multilayer adsorption. The Temkin isotherm assumes that the decrease in the heat of adsorption is linear rather than logarithmic, as in the Freundlich model. In Temkin, the heat of adsorption of all molecules in the adsorbed layer should decrease linearly with coverage from adsorbed/adsorbent interaction. The Dubinin-Radushkevich isotherm, like the Freundlich model, assumes a heterogeneous surface [16].

The Langmuir equation (Equation 5) was applied to the adsorption equilibrium at different adsorbent doses as:
\[
q_e = \frac{b Q_{\text{max}} C_e}{1 + b Q_{\text{max}}}
\]  
(5)

\[
\frac{C_e}{q_e} = \frac{1}{Q_{\text{max}} b} + \frac{C_e}{Q_{\text{max}}}
\]  
(6)

where \(C_e\) is the concentration of dye in solution at equilibrium (mg/L); \(q_e\) is the amount of dye adsorbed by 1 g of adsorbent at equilibrium (mg/g); \(Q_{\text{max}}\) is the maximum adsorption capacity of the adsorbent; and \(b\) is the constant for the binding energy of the adsorption system. The equation describing the Freundlich model is:
\[
q_e = K C_e^n
\]  
(7)

Its logarithmic form was applied to the adsorption equilibrium at different adsorbent doses as:
\[
\log q_e = -\frac{1}{n} \log C_e + \log K
\]  
(8)

where \(K\) and \(n\) are Freundlich constants and are relative indicators of adsorption capacity and adsorption intensity, respectively. A favorable adsorption condition is achieved when \(n>1\). The Temkin isotherm applied was:
\[
q_e = \frac{RT}{b} \ln(a C_e)
\]  
(9)

where \(b\) is the Temkin constant for heat of adsorption (kJ/mol); \(R\) denotes the gas constant (0.0083 kJ K⁻¹ mol⁻¹); \(a\) is the Temkin isotherm constant (l/g); and \(T\) is the absolute temperature (K).

The equation describing the Dubinin–Radudshkevich model is:
\[
q_e = q_D \exp(-B_D E_D^2)
\]  
(10)

In which \(ED\) (Polanyi potential) is calculated by:
\[
E_D = RT \ln\left(1 + \frac{1}{C_e}\right)
\]  
(11)

Where \(q_D\) is the adsorption capacity of the adsorbent (mg g⁻¹); \(q_e\) is the amount of metal adsorbed at equilibrium (mg g⁻¹); and \(BD\) denotes a constant for the adsorption energy (mol² KJ⁻²). The mean energy of adsorption can be calculated as:
\[
E = \frac{1}{\sqrt{2B_D}}
\]  
(12)

The magnitude of \(E\) suggests a mechanism for the adsorption process. In fact, when \(E\) is 8-16 KJ mol⁻¹, an ion exchange mechanism can be considered. The dominant mechanism is physisorption for the chemisorption and ion exchange mechanisms when \(E\) is less than 8 KJ mol⁻¹.

The corresponding adsorption isotherm constants and correlation coefficients are presented in Table 3. This table shows the coefficients for the linearized form of the isotherm model for adsorption. Negative values for slope and intercept in the Langmuir and Freundlich linearized forms indicate the inadequacy of these isotherm models to explain adsorption. The data was reasonably well-fitted to the Freundlich model, indicating heterogeneous surface binding. These isotherm equations were compared by calculating the correlation coefficient. The adsorption isotherm data for AZ were well-described by the Langmuir isotherm. In contrast, this isotherm could not adequately explain the adsorption process for the other adsorbents. The adsorption data for AZ and TNP in dye concentration 10 indicates they are better described by the Temkin isotherm; however, the DF data fit well with the Dubinin-Radushkevich model.

**Conclusions**

This study confirms the potential of treated newspaper pulp, Azolla filiculoides, and date fibers for removal Rhodamine 6G from aqueous solutions. Under optimized conditions for pH of the aqueous sample solution (6), time (30 min) and adsorbent dose (0.3 g/45 mL of sample solution), the amount of the adsorbed R6G was 75%-95% at 25°C. It was found that the adsorption process for all adsorbents well fit the pseudo-second order kinetic model. The isotherm of the equilibrium data of the adsorption of R6G onto Azolla filiculoides was well-defined by the Langmuir model. Sreelatha and Padamja [17] were used Palm shell powder as sorbent for removal of R6G. The batch
studies clearly demonstrated that there was >94 % removal for the dye concentrations equals to 600 mg/L. The kinetic and isotherm results were comparable to the results obtained in this study.

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