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Preparation of bio-silica/chitosan nanocomposite for adsorption of a textile dye in aqueous solutions

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ABSTRACT

The aim of this study was to evaluate the efficiency of immobilized nanosized bio-silica (average crystalline size of 20 nm) within chitosan as a nanocomposite adsorbent for removing Acid Red 88 (AR88) in aqueous phase. As result, the amount of adsorbed AR88 (mg g^{-1}) was increased with increasing reaction time and adsorbate concentration and decreasing temperature and initial pH. A rapid increment in the adsorption was happened with increasing adsorbent dosage from 1 to 3 g l^{-1}, while further increment in the adsorbent dosage resulted in an insignificant increase in the adsorption (1.66 mg g^{-1}). The kinetic study was performed and the results indicated the suitability of pseudo-second order kinetic model (R^2 = 0.994). Besides, the correlation coefficient of Elovich model confirmed chemical nature of the adsorption (R^2 = 0.9756). The fitness of experimental data to the intra-particle diffusion model demonstrated that the adsorption process occurred via a multi-step mechanism. But, the intra-particle diffusion was not the sole rate-limiting stage. According to the Langmuir isotherm model (R^2 = 0.9962), the maximum adsorption capacity of bio-silica/chitosan nanocomposite for sequestering AR88 was about 25.84 mg g^{-1}. In addition, negative ΔG° and ΔH° values obtained through thermodynamic study indicated that the adsorption of AR88 onto nanocomposite was simultaneous and exothermic in nature, respectively.

1. Introduction

There are several industries discharging organic dyes in aqueous environments such as textile, clothing, dyestuff, leather, plastic, paper, food processing and cosmetic (Monvisade and Siriphannon, 2009; Zhu et al., 2010, 2011a; Nesic et al., 2012). The presence of organic dyes in aqueous environments is one of the serious environmental problems because of the toxicity of organic dyes to aquatic life and low biodegradability in such environments (Monvisade and Siriphannon, 2009; Nesic et al., 2012). In addition, organic dyes can be identified as the carcinogenic substances (Zarezadeh-Mehrizi et al., 2013). Many technologies have been applied for removing organic dyes from aqueous solutions including biological degradation, adsorption, membrane technologies, coagulation–flocculation, electrochemical techniques and advanced oxidation processes (Karaca et al., 2008, 2013). Among aforementioned techniques, adsorption method using solid adsorbents has been found to be a promising technique for removing organic dyes in terms of its simplicity, insensitivity to toxic environments, cost-efficiency and ease of operation (Karaca et al., 2008; Zhu et al., 2010). The application of activated carbon as the most widely used adsorbent has become limited because of its high cost and the need for regeneration (Selvam et al., 2008; Copello et al., 2011; Silva et al., 2012). Therefore, in recent years, the application of cheap and locally available adsorbents such as clay minerals has been considered (Zhu et al., 2010). Silica based materials would be favorable to adsorb various pollutants because of the capability of their functional groups for the attachment of target pollutants (Mahmoud and Al-Bishri, 2011; Rostamian et al., 2011; Najafi et al., 2012; Gomes et al., 2013). The applicability of silica for the adsorption of organic dyes has been evaluated previously (Zarezadeh-Mehrizi et al., 2013). Among various silica containing materials, diatomaceous earth, also known as bio-silica, is a siliceous biological sedimentary rock with a porous structure consisting of 87–91% silicone dioxide which can be used as an

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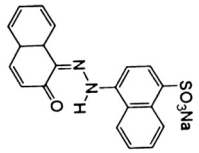
Table 1
Characteristics of the studied azo dye.

Color index name	Chemical structure	Molecular formula	M_w (g mol^{-1})	λ_{max} (nm)
Acid Red 88 (AR88)		$C_{20}H_{13}N_2O_4SNa$	400.38	507

alternative adsorbent for removing organic dyes from aqueous media due to its high surface area along with functional groups (Zhu et al., 2011b; Dang et al., 2013). However, it is difficult to withdraw fine adsorbents such as bio-silica with nanosized crystal from aqueous solutions; thus, one effective alternative to overcome this problem is to find a suitable support for the immobilization of adsorbent. This approach improves mechanical strength of the adsorbent and leads to increasing mass density and the retention time of the adsorbent within the reactor. Moreover, immobilization is an essential step for the scale-up of the adsorption process (Copello et al., 2011; Zhao et al., 2011; Khorramabadi et al., 2012). The application of polymeric matrixes such as alginate, chitosan and various resins is one of the most widely used techniques for the immobilization (Zhao et al., 2011; Karim et al., 2012; Khorramabadi et al., 2012). Chitosan is a suitable natural biopolymer for the immobilization process because of its hydrophilicity, biodegradability, non-toxicity and availability (Chang and Juang, 2004; Cestari et al., 2008; Wan Ngah et al., 2011). Chitosan is the second most plentiful biopolymer in nature (Zhou et al., 2011; Zhu et al., 2011a). In addition, adsorption capacity of the chitosan for sequestering anionic dyes due to the electrostatic attraction between the protonated amine groups on the chitosan and the sulfonic groups of the anionic dyes would be beneficial to enhance the adsorption of anionic dyes together with the immobilized adsorbent (Chang and Juang, 2004; Zhou et al., 2011; Zhu et al., 2011a). The aim of the present study was to prepare bio-silica/chitosan nanocomposite and evaluate its adsorption capacity for the adsorption of an anionic dye (Acid Red 88) in aqueous solutions. To the best of our knowledge, there is no report on the application of bio-silica/chitosan nanocomposite for the adsorption of textile dyes such as Acid Red 88 (AR88) in aqueous solutions.

2. Materials and methods

2.1. Materials

Bio-silica and chitosan, which were of analytical grade, were purchased from Sigma–Aldrich, USA. The dye was purchased from Nasaj Sabet Company, Iran and used as received. The characteristics of the dye are shown in Table 1. All reagents and chemicals were of analytical grade purchased from Merck, Germany. To prepare bio-silica/chitosan nanocomposite, first chitosan (10 g) was dissolved in 1000 ml of 1 M acetic acid and mixed using magnetic stirrer (Heidolph MR 3001, Germany) at 100 rpm for 2 h. Then, bio-silica (5 g) was added to the concentrated solution and magnetically stirred for 1 h to reach homogeneity. The resulted mixture was kept for 8 h in a stable place to obtain a bubble-free mixture. The weight ratio of chitosan to bio-silica was 2:1 for all of the sample preparation procedures. The viscous mixture was added dropwise via a syringe to a 500 ml solution containing 15% NaOH and 95% ethanol. The volumetric ratio of NaOH/ethanol was 4. Then, they were stored in the solution for 24 h to allow the nanocomposite beads to be formed. The resulted beads was withdrawn from the solution and washed with deionized water several times to remove impurities (Chang and Juang, 2004; Hasan et al., 2008). The obtained beads were dried in room temperature until constant weight. Finally, dried form of the beads was crushed, sieved and particles between 20 and 40 mesh size were applied for the adsorption of AR88 in experiments.

2.2. Experimental procedure

The experiments were carried out in 100 ml Erlenmeyer flasks as batch experimental reactors to investigate the effects of the reaction time, adsorbent dosage, mixing speed, temperature, initial pH and the initial dye concentration on the dye adsorption efficiency. A shaker incubator (Model: ISH 554D, Fannavarane Sahand Azar, Iran) was used for mixing the flasks containing AR88 and to evaluate the effect of temperature on adsorption process. The pH was adjusted to the desirable values with 0.1 M HCl and 0.1 M NaOH at the beginning of each experiment. In a typical manner, the efficiency of different adsorbents (pure bio-silica, pure chitosan and bio-silica/chitosan nanocomposite) was compared to choose suitable adsorbent for the adsorption of AR88 in aqueous phase. This set of experiment was conducted at an initial dye concentration of 50 mg l^{-1}, adsorbent dosage of 3 g l^{-1}, adjusted temperature of 273 K, initial pH of 7 and mixing speed of 100 rpm for 60 min. Then, the experimental procedure was systematically performed according to Table 2 using bio-silica/chitosan nanocomposite as selective adsorbent. To determine the adsorption of dye in absence of the adsorbent, a control flask without adsorbent was used. All experiments were carried out twice to check the accuracy of the obtained data. Then the mean values were written down.

2.3. Analysis

The initial pH was measured by a Metrohm pH meter (Model: 654, Germany). At the end of each experiment, the supernatant was withdrawn and centrifuged for 5 min at 6000 min^{-1}. The residual

Table 2
Experimental design for the adsorption of AR88 onto bio-silica/chitosan nanocomposite.

No.	Parameter	Operational parameters					
		Reaction time (min)	Adsorbent dosage (g l^{-1})	Mixing speed (rpm)	Temperature (K)	Initial pH	Dye concentration (mg l^{-1})
1	Reaction time	10–240	3	100	298	Neutral	50
2	Kinetic study	10–120	3	100	298	Neutral	50
3	Adsorbent dosage	120	1–6	100	298	Neutral	50
4	Mixing speed	120	3	50–250	298	Neutral	50
5	Temperature	120	3	50	298–328	Neutral	50
6	Thermodynamic study	120	3	50	298	Neutral	50
7	Initial pH	120	3	50	298	3–11	50
8	Initial dye concentration	120	3	50	298	Neutral	10–400
9	Isotherm study	120	3	50	298	Neutral	10–400