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Enhanced removal of crystal violet by low cost alginate/acid activated bentonite composite beads: Optimization and modelling using non-linear regression technique

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Adsorption feasibility of crystal violet dye (CV^+) onto acid-activated bentonite clay, entrapped in a polymeric matrix of calcium alginate bead examined in this work. Operational parameters have been investigated, isotherms were analyzed using non-linear regression model and data obtained optimized by Box–Behnken model. Pseudo-*n*th order fits well with the kinetic data obtained, and the reaction order *n* was found to be between 0.925 and 3.269. Desorption tests showed that the recovery of CV^+ decreased from 92.39 to 84.59% in the tenth cycle. The maximum adsorptions of crystal violet onto alginate/acid activated bentonite beads (A-AAB), alginate/bentonite beads (AB), and acid activated bentonite clay (AAB) were 582.4, 498.2 and 229 mg dye g^{-1} respectively. The thermodynamic parameters indicate that the adsorption process of CV^+ is endothermic and more effective at high temperatures.

1. Introduction

Dye polluted waterways from rapidly growing industrial activities have become a threat to the public since the dyes can inflict life-threatening diseases and also devalue the aesthetic nature of the water bodies, leading to abnormal variations in the aquatic ecosystem [18,20,28,40]. The discharge of extremely tiny amounts of dyes even at minimum concentrations may be toxic and difficult to decolourize due to their complex structure [36,40,51,60]. Thus, treatment of coloured wastewater is a major concern for the environmentalists. Crystal violet belongs to the triphenylmethane dyes class and is used largely as histological stain in veterinary medicine, as bacteriostatic agent and skin disinfectant in the medical community [40]. Crystal violet is harmful when ingested or inhaled and can cause life-threatening injury to the conjunctiva, skin irritation and permanent blindness [2,40,49]. The harmful effects of CV^+ warrant it removal from industrial wastes prior to discharge into water bodies and this has motivated us to take up research for its removal from wastewaters. Overtime, adsorption has been adopted as a suitable and superior technique for dye removal, due to its simplicity, ability to treat trace amount of dyes and regeneration capability [19]. Other known techniques such as biochemical degradation, photodegradation and electrocoagulation have been utilized, but these techniques are time consuming, expensive possess some drawbacks [9,30,31]. Many adsorbents had been used previously such as activated carbon, and showed high adsorption capacity and good surface reactivity but its regeneration results in 9–14% loss and decreased uptake capacity [16]. Other low cost adsorbents have been exploited for dye removal such as papaya seeds, orange peel, banana peel and saw dust [1,5,21,25,27,39], but there is a need for more efficient, abundantly available and low cost eco-friendly adsorbents with high adsorption capacity to be utilized for this purpose, and this is a prominent concern for the researcher and environmental technologists.

Clays are being considered as alternative inexpensive adsorbents and have been applied widely in various fields of adsorption science due to their eco-friendliness, non-toxicity and availability [14,22,42,54]. Bentonite has been utilized in this work due to its remarkable adsorption properties compared to other clays. Bentonite is natural clay composed of octahedral sheets of aluminium ions situated between two tetrahedral sheets of silicon ions [14]. The substitutions of Al^{3+} for Si^{4+} within the lattice structure and Mg^{2+} for Al^{3+} in the octahedral sheet result in negative charges on the clays and, high adsorption for the dyes in aqueous solutions by the exchangeable cations [13,14,15,54]. However, it is difficult to separate the suspended bentonite solid

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from aqueous solution after adsorption of dyes [45]. In order to solve this problem, it is required to bind bentonite with a biopolymer. Biopolymer/clay composites have attracted considerable attention as they demonstrated excellent combined properties compared to the pure materials [11]. The surface property of the bentonite in this work has been modified with HCl so as to improve the dye adsorption capacity of the clay material. Moreover, encapsulation of the acid activated bentonite into alginate, an eco-friendly copolymer of α-L-glucuronic acid and β-D-mannuronic acid could improve the adsorbent structural integrity and widen its application [11]. Previous reports on crystal violet adsorption onto various adsorbent indicated low adsorption capacity and, some of the adsorbents are difficult to separate from the aqueous solution after adsorption [7,12,33,35,41,52,53,59].

The objective of the present work was to design recoverable spent adsorbent from treatment plant and thus, to investigate the adsorption capacity and effectiveness of alginate/acid activated bentonite composite beads (A-AAB) in removing crystal violet dye (CV^+) from aqueous solution. Various adsorption parameters were examined, and the data obtained were modelled and optimized to provide useful information to environmental scientists/engineers for designing effective and low cost wastewater treatment plants.

2. Materials and methods

All reagents used were of analytical purity. Alginic acid (Alfa Aesar), calcium chloride, sodium hydroxide and commercial grade bentonite were obtained from Sigma–Aldrich and used without further purification. Reagent-grade HCl (Reidel-de Haen) was used for acid activation of bentonite. The basic dye, crystal violet (CI = 42,555, dye content ≥90%, molecular formula $C_{25}H_{30}Cl$, MW 407.98 and λ_{max} = 590 nm) was obtained from Sigma–Aldrich and used without further purification. Distilled water was used for preparation of all experimental solutions.

2.1. Preparation of acid-activated bentonite clay (AAB)

Ten grams sample of natural bentonite was soaked in 50 mL of 2 M HCl acid for 24 h at 30 °C in a flask. The acid activated sample was washed thoroughly with distilled water until the pH of the solution was 5 and dried at 100 °C in the oven for 3 h prior to use.

2.2. Preparation of alginate/acid activated bentonite beads (A-AAB)

Sodium alginate solution (1%, w/w; V = 100 mL) was prepared by dropwise addition of the pre-calculated amount of NaOH into alginic acid solution. The composite beads were prepared via ionic gelation technique described elsewhere [11,51]. Two grams of AAB was dispersed in distilled water, the prepared alginate solution was added, and the mixture was stirred for 3 h. The homogenous mixture was filled into a syringe and dropped through the syringe needle into a flask containing 100 mL $CaCl_2$ (3%, w/v) as the gelling solution. After 24 h, the beads were collected from the solution and washed severally with distilled water using a 100 μm mesh sieve before use.

2.3. Adsorption studies

Adsorption of crystal violet onto A-AAB, AB and AAB were investigated in a batch mode system. Adsorption studies were conducted at 200 rpm by mechanical agitation at 25 ± 1 °C for 6 h. Different amounts of beads (10–100 mg) in 25 mL solution initially containing 50 mg L^{-1} of CV^+ dye were utilized in the experiment. The influence of pH on the adsorption capacity of the beads was examined over pH range 4.0–10.0 at 25 °C, the pH was varied without altering the CV^+ concentration significantly by using little amounts of concentrated HCl and NaOH solutions. NaCl varied between 0.2–1.0 mol L^{-1} was employed as electrolyte to examine the effect of ionic strength on CV^+ adsorption. The initial concentration of CV^+ was varied between 25 and 100 mgL^{-1} to investigate the beads adsorption capacity at pH 8.0. Adsorption was also studied at varying temperatures (15–60 °C) to investigate the temperature effect and analyze the thermodynamic mechanism. Averages of triplicate experiments were reported for each adsorption studies, determined using UV/VIS Spectrophotometer (Beijing, T80+) and the amount of adsorbed dye and adsorption percentage were obtained respectively as follows:

$$q_e = (C_o - C_e)\frac{V}{m} \tag{1}$$

$$R = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o initial concentration of the CV^+ (mg L^{-1}), C_e the equilibrium concentration of CV^+ (mg L^{-1}), m mass of the adsorbent (mg), V the volume of CV^+ (L) and R is the percentage removal.

2.4. Desorption and recycling of adsorbent

The reusability and efficiency of the low cost A-AAB beads were investigated. Consecutive adsorption–desorption cycles were obtained under suitable batch system 10 times with 0.1 mol L^{-1} H_2SO_4, NaOH, Na_2SO_4, HNO_3 for 6 h. The loaded beads were immersed in the desorption solution and agitated at 200 rpm for 6 h at 25 ± 1 °C. After each cycle, the final CV^+ concentration was determined as mentioned above, and the percentage desorption was calculated as follows:

$$D = \frac{m_y}{m_x} \times 100 \tag{3}$$

where, m_y (mg) and m_x (mg) are the amounts of desorbed and adsorbed CV^+ respectively.

2.5. Characterization of composite beads

The infrared spectra of Alginate, A-AAB and dye-loaded beads were analyzed using Fourier transform infrared (FTIR) spectroscopy (PerkinElmer FT-IR model 65 spectrometer) in the range of 4000–400 cm^{-1}. The point of zero charge (pH_{pzc}) of the samples was also investigated by pH-drift method [61]. The diameter of the beads was determined by taking digitized images of 30 beads and analyzed with shape-recognition software (KS300 Carl Zeiss, Germany). The specific surface areas (S_{BET}) of the beads were calculated using Brunauer–Emmet–Teller (BET) equation from N_2 adsorption–desorption isotherms at 77 K (liquid nitrogen temperature) by surface analyzer (NOVA 1000, Quantachrome).

2.6. Design and optimization of parameters

Batch adsorption process can be optimized and designed using isotherm, and kinetic equations [3,4], and the aim of this optimization is to develop efficient and simple adsorption process. The effect of adsorption process parameters such as adsorbent dose, initial CV^+ concentration and pH on the removal efficiency of CV^+ onto A-AAB was determined using Box–Behnken design (BBD). The BBD model was used to investigate the combination of parameters that will give optimum removal efficiency of CV^+. Each adsorption parameter has 3 levels designated as +1, 0 and −1 for high, middle and low values, respectively as shown in Table 1. In the model, dose of A-AAB, pH and initial concentration of CV^+ were