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ORIGINAL ARTICLE

Calcium hydroxide as low cost adsorbent for the effective removal of indigo carmine dye in water

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Abstract Adsorption of indigo carmine dye onto calcium hydroxide was investigated in this work. The variation in the pH, adsorbent dose, dye concentration, duration and the temperature was evaluated. Adsorption of indigo carmine dye onto calcium hydroxide was effective at pH 12 (50 min) and follows Langmuir-type isotherm behaviour. The adsorption process follows pseudo-second order rate kinetics. Enthalpy, entropy, free energy and the activation energy parameters have been reported.

1. Introduction

Several million tons of different types of synthetic dyes are manufactured every year across the world [1,2]. The characteristic features of the synthetic dyes can be altered by substituting a suitable functional group to the dye [3]. Dyes have been classified into azo dyes, phthalocyanine dyes, VAT dyes (which bind the substrate in basic medium), cationic dyes and anionic dyes (which attain the charge in aqueous medium), insoluble dispersive dyes, reactive dyes, indigoid dyes etc. Textile, paper and pulp, food processing and technology, dye sensitized photovoltaics, leather processing and tanning industries utilize large quantities of synthetic organic dyes as colourants [4–8]. During the synthesis and application of dyes, large quantities of untreated dyes are discharged into the environment. Indigo carmine is one of the most common dyes used in textile, medical and pharmaceutical applications [9,10]. Discharge of indigo carmine into the environment is hazardous and causes skin related diseases, affects the cornea and exhibits cytotoxicity [11–13]. It has been found that a majority of the dyes cannot be practically treated effectively prior to their release into the environment. Traditional methods to treat the water were found to be ineffective due to the complex nature of the dyes and their reactivity [14]. Several methods and techniques have been developed for the treatment of dye effluents. Chemical, biological and physical methods have been developed [15–18]. The chemical methods involve precipitation, oxidation, chemisorption, and photocatalysis [11,12,19,20].

Even though the efficiency of the chemical methods is high, scalability is a major hurdle. Biological methods involve

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microorganisms, fungi and enzymes for the degradation and decolourization of dyes [21]. Bulk methods have also been employed for the removal of indigo carmine dye in waste water [22]. Electrocoagulation, electroflocculation, electrochemical precipitation routes have also been employed but they are energy intensive [23–25]. When compared to the above methods, physical methods of treatment of dyes were found to be economically and technologically simple and easy to handle. Adsorption is one such method in which synthetic dyes will adsorb onto the solid substrate during the treatment of dyes. Metal oxides, agrowaste, chitosan, cross-linked polymers, zeolite, coal fly ash, alumina, calcium oxide, cynodon dactylon have been used as adsorbents for the removal of indigo carmine dye [13,26–28]. Agrowaste is one of the cheap materials which is abundantly available that can be used to treat indigo carmine dye but its adsorption efficiency is poor [29]. It is desirable for any adsorbent to be cheaper, easy to handle, environmentally benign, possess high greater affinity for the dyes, highly efficient and regenerative. There is no universal adsorbent, which can be used for the effective removal of different types of dyes. Recently we had reported the removal of indigo carmine using magnesium oxide as an adsorbent and the efficiency is more than 90% [30]. This promotes us to explore new adsorbent i.e. calcium hydroxide for the removal of indigo carmine dye. In this work, we used calcium hydroxide as a low cost adsorbent to examine its effectiveness on the adsorption of indigo carmine dye by varying different parameters such as pH, dose, concentration, temperature and analysed the nature of adsorption process.

2. Experimental section

Calcium hydroxide and indigo carmine dye were purchased from SD-Fine Chemicals, India and used without purification.

2.1. Preparation of indigo carmine dye solution

Indigo carmine dye stock solution was prepared by dissolving 50 mg of indigo carmine dye in 1000 mL of distilled water. A series of dye concentrations in the range of 1.0721×10^{-5} M to 1.0721×10^{-4} M or 0.50 mg to 5.0 mg/100 mL were further prepared by transferring 10 mL, 20 mL, 30 mL, 40 mL, 50 mL and 100 mL of the dye solution into a standard flask followed by dilution to 100 mL using distilled water. The pH of the indigo carmine dye solution was adjusted using either 1 M HCl or 1 M NaOH (pH = 3, pH = 6, pH = 9, pH = 12) to test the effect of pH on the adsorption of dye on calcium hydroxide.

2.2. Adsorption measurements

Kinetic experiments for the adsorption of indigo carmine dye solution on calcium hydroxide was carried out by adding 0.1 g of calcium hydroxide in 100 mL of indigo carmine solution of known concentration (5 mg/100 mL) at room temperature (25–28 °C).

The effect of temperature on the adsorption of indigo carmine dye solutions (at different pH, dosage −0.1 g) was measured. The effect of temperature as a function of time (10, 20, 30, 40, 50 min) on the dye removal was also examined at a predetermined equilibrium conditions i.e. pH = 12, dose of calcium hydroxide −0.1 g. The duration at which equilibrium state is attained was estimated to determine the effectiveness.

The maximum absorption was observed at 600 nm and the entire adsorption measurements were performed at 600 nm. Batch experiments were performed by varying the adsorption conditions. Concentrations of the dye solutions after adsorption were monitored using colorimeter (CL-63 model).

2.3. Adsorption isotherms

Batch adsorption isotherm studies were conducted to determine the different adsorption isotherm models. The adequacy of the different models will be evaluated to determine the adsorption process. For adsorption isotherms, indigo carmine solutions of different concentrations ranging from 0.5 to 5 mg/L (1.0721×10^{-5} M to 1.0721×10^{-4} M) were examined by adding different quantities of calcium hydroxide (0.025 g, 0.05 g, 0.075 g, 0.1 g).

Calcium hydroxide sample was characterized using a Bruker D-8 Advanced X-ray powder diffractometer with Cu $K\alpha = 1.5418$ Å, scan rate 2° min^{-1} (steps: 0.02°); scan range of 10–55°.

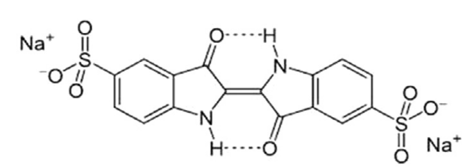
The crystallinity of the sample was examined by comparing the data with the international centre for diffraction data. Elico CL-63 colorimeter was used for the measurements. The filters used for the measurements is λ_{max} = 600 nm up to pH 12 (blue colour). At pH 13, the solution of indigo carmine dye will exhibit yellow colour.

3. Results and discussion

The structure of indigo carmine dye ($C_{16}H_8N_2Na_2O_8S_2$) is shown in Fig. 1. The reflections in the powder X-ray diffraction pattern of calcium hydroxide was indexed to hexagonal system with the space group P-3m1 (see Supplementary Fig. 1). The average crystallite size of calcium hydroxide was calculated using Scherrer formula and is in the range of 30–50 nm [31]. The relativity involving the removal of indigo carmine as a function of pH, dye concentration, temperature and time with the adsorbents was considered to validate the rate of dye removal.

3.1. Effect of pH

The effect of initial pH of dye solution on the percentage of removal of alizarin red was investigated by maintaining the solution pHs at 3, 6, 9 and 12 and the data are shown in Fig. 2. It has been observed that adsorption of indigo carmine on calcium hydroxide is maximum at pH 12.



Structure of sodium salt of indigo carmine dye

Figure 1 Structure of indigo carmine dye.