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Decolorization and detoxification of Acid blue 158 dye using cuttlefish bone powder as co-adsorbent via photocatalytic method

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ABSTRACT

The photocatalytic removal of Acid blue 158 (AB 158) dye from aqueous solutions using cuttlefish bone powder (CFBP) as co-adsorbent has been carried out. Both photocatalytic and adsorption studies were compared on the decolorization of AB 158 by studying the effect of various equilibrium parameters like contact time, dose of catalyst and adsorbent, pH and concentration variation. Both the sorption and photocatalytic studies were pH and concentration dependent. Maximum efficiency was achieved at pH 2.0. As a co-adsorbent, CFBP enhanced the photocatalytic activity of TiO_2 which is mainly due to the adsorption of AB 158 dye on CFBP which is followed by the transfer of dye to the TiO_2 surface, where it undergoes photocatalytic decoloration. The presence of functional groups, surface morphology and crystalline nature of the prepared sorbent were confirmed by Fourier Transform Infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The detoxification of AB 158 dye was examined by chemical oxygen demand (COD) method. The kinetics of photocatalytic decolorization of AB 158 dye using CFBP/TiO_2/UV followed Langmuir–Hinshelwood mechanism.

1. Introduction

Synthetic dyestuffs in industrial effluents are toxic to creatures in water. Many industries use dyes and pigments such as those involving textiles, dyeing, and papermaking, discharge large amounts of colourful materials in their wastewater. Because these effluents can cause adverse effects such as allergic dermatitis, skin irritation, cancer, and mutation [1], it is imperative to remove these dye pollutants from bodies of water. Water pollution by dyes is a worldwide problem particularly in textile industry where large quantities of dye effluents are discharged from the dyeing process. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff being produced annually across the world [2]. It is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent [3]. Water soluble dyes such as acid dyes and reactive dyes are not easily removed in conventional physicochemical coagulation methods, and are not biodegradable [4]. Coagulation, flocculation [5], ozonation [6] and adsorption [7] are found to be well known treatment methods for the treatment of wastewater. Yet there is another problem associated with the coloured wastewater which is mainly due to the presence of huge amount of organics in the dye molecules, as most of the conventional treatment methods fail to remove them from wastewater.

Adsorption has been identified as one of the best methods for the removal of dyes from water and wastewater owing to its simplicity of design, insensitivity to toxic substances, ease of operation and low maintenance [8]. Many investigations have been done on the feasibility of low cost material, as the sorbent for removal of various dyes from wastewater including: waste coir pith [9], modified clays [10], oxihumolite [11], fly ash [12], Na-bentonite [13], kaolinite [14], giant duck weed [15], eolith [16], chitosan [17], powdered peanut hull [18] and using carbon as co-adsorbent in photocatalytic degradation methods [19].

The recent trend in treatment of organics and dyes has shifted from phase transfer to destruction of pollutants, i.e., advanced oxidation process. Advanced oxidation processes are of interest currently for the effective oxidation of a wide variety of organics and dyes. Among them, top priority goes to photocatalytic degradation. Most of the photocatalytic detoxification studies of water use TiO_2 as the photocatalyst [20], due to its strong oxidizing power, non-toxicity, inertness, inexpensive and long term photo-stability. The initial step in the TiO_2-mediated photocatalysed degradation is proposed to involve the generation of an electron/hole pair leading to the formation of hydroxyl radicals and super

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oxide radical anions, which are very strong oxidants [21]. Both valence band holes and hydroxyl radicals are powerful oxidizing species which in turns lead to complete oxidation of organic pollutants into carbon dioxide, water and some mineral acids in a few hours. Thus, showing the significance of photocatalytic degradation process. However, recently some studies have been carried out to evaluate the efficiency of photocatalysts using TiO_2 with activated carbon as co-catalyst [19,22,23]. A synergetic effect has been observed by using powdered TiO_2 and powdered activated carbon in the photocatalytic degradation of organic pollutants. This synergetic effect has been ascribed to the presence of a common contact interface spontaneously created between both solids [24].

Cuttlefish bone is abundant, cheap and rich in calcium. Cuttlefish possess an internal structure called the cuttlebone. As it is porous, it provides the cuttlefish with buoyancy which can be regulated by changing the gas-to-liquid ratio in the chambered cuttlebone. Traditionally, cuttlebones are used by jewellers and silversmiths as moulds for casting small objects. They are possibly better known today as the hard material given to parakeets and other cage birds as a source of dietary calcium [25].

Only a few studies have been carried out using CFBP as adsorbent for water and waste water treatment. Ben Nasr et al. studied the efficiency of cuttlefish bone in removing fluoride from water [26]. The removal efficacy of the Reactive blue dye using cuttlefish bone powder was found to be 60%, 45%, 37.5% and 31.9% at a time interval of 3 h and the initial dye concentrations of 25, 50, 75 and 100 mg/l, respectively [27].

The goal of this research was to investigate the feasibility of using cuttlefish bone powder as adsorbent in the adsorption technique and as a co-adsorbent in the photocatalytic decoloration technique for the removal of AB 158 dye from aqueous solutions. Various conditions like effect of contact time, pH, dose and initial concentration were optimized. The kinetic study was carried out by Langmuir–Hinshelwood mechanism. Papers devoted to removal of the dyes by TiO_2 as photocatalyst and CFBP as co-adsorbent in presence of UV light irradiation have seldom been reported. This study therefore investigates the adsorption characteristics and photocatalytic activity of CFBP/TiO_2/UV for the decolorization of dyes from aqueous solution under various experimental conditions. The detoxification of AB 158 dye was also studied by determining the initial and final COD of the solution that was irradiated under optimized conditions.

2. Experimental

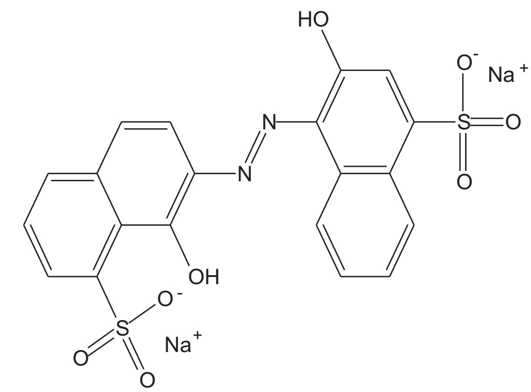
2.1. Materials used

Cuttlefish bone powder was prepared from cuttlefish bone. It is available in the seashore areas and for the present study it has been collected from Rameswaram seashore. Titanium dioxide was purchased from CDH, Mumbai. Acid Blue 158 (AB 158) was obtained from M/s Sree Chemidyes (India), Bangalore and was used as such without further purification, for colour removal study. Properties of AB 158 are given in Table 1. NaOH, HCl, glacial acetic acid, glutaraldehyde were purchased from Merck chemicals and all other chemicals and reagents were of analytical grade.

2.2. Preparation of cuttlefish bone powder (CFBP)

Cuttlebones are the skeletons of the cuttlefish. The major component of cuttlefish bone is calcium carbonate (85%). This is also the major component in eggshells. The next major component is organic material (8.9%), probably mainly carbohydrate material. The nitrogen content of 8300 mg/kg indicates that approximately 20% of the organic material is proteinaceous. 1.4% of acid-insoluble material is silicate (sand). The remaining elements are all trace elements. Cuttlefish bone was cut into small pieces and immersed in double distilled water to remove dirt and boiled for 10 min to desorb any impurities, dried at 103° to 105 °C for 24 h and allowed to cool in a dessicator, crushed and sieved to get uniform size of CFBP [26].

Table 1
Properties of dye.

C.I number	CI-14880
C.I name	Acid blue 158
Application class	Acid
Ionization	Acidic
Solubility aqueous (%)	Very high
Colour	Blue
Molecular structure	
Formula weight	518.43 g/mol
Wavelength	633 nm

2.3. Characterization and analysis

The prepared sorbents were characterized by FTIR spectra of the samples as solid by diluting in KBr pellets were recorded with JASCO-460 plus model. The results of FTIR spectrometer were used to confirm the functional groups present in the CFBP, TiO_2 and CFBP/TiO_2. The surface morphology of the CFBP before and after dye sorption was studied with scanning electron microscope (SEM) with Vega3 Tescan model. The phase and purity of CFBP was confirmed with X-ray diffraction (XRD) analysis. Computations were made using Microcal Origin (Version 6.0) software. pH_{ZPC} of the sorbents were measured using pH drift method.

2.4. Adsorption studies

To study the effect of parameters such as contact time, sorbent dosage and pH for the decolorization of AB 158 by CFBP, batch studies were carried out in a mechanical shaker at a constant speed of 200 rpm at room temperature. The adsorption isotherm experiment was carried out by agitating 50 mL dye solutions of various concentrations with the sorbent in a thermostated shaker. After agitation, the dye solutions were filtered and were measured using a UV–vis spectrophotometer (Pharo 300 Merck) at 633 nm. pH measurements were carried out with expandable ion analyzer EA 940 and pH electrode. The extent of dye removal was studied by optimizing various conditions like contact time, pH of the medium, dose of adsorbent, and initial concentration of adsorbate. The dye removal percentage was calculated using the following relationship.

$$\text{Dye removal}\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$