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Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material De-oiled Soya: Isotherm, kinetics and bulk removal

Alok Mittal *, Damodar Jhare, Jyoti Mittal

Department of Chemistry, Maulana Azad National Institute of Technology, Bhopal 462 051 India

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ABSTRACT

The main focus of this research is to develop a systematic method for the removal of a hazardous dye Eosin Yellow from its aqueous solutions by adsorption process. Eosin Yellow is an anionic halogen containing dye which belongs to Flouorescein class. During the batch studies it has been found that Eosin Yellow showed a decrease in adsorption over De-oiled Soya with increasing pH, while increase in concentration, temperature, amount of adsorbent and sieve size increased the adsorption of the dye over De-oiled Soya. The ongoing adsorption follows Langmuir, Freundlich, Tempkin and D–R adsorption isotherm models. On the basis of Langmuir constant values like Gibb's free energies at 30, 40 and 50 °C have been found as 23.43, 25.15 and 25.23 kJ mol^{-1} respectively, while enthalpy and entropy of the adsorption process were calculated as 3.598 kJ mol^{-1} and 66.277 JK^{-1} mol^{-1}, respectively. Kinetic studies reveal that pseudo second order kinetics is operative during the adsorption process and the rate constant for the process was close to 1×10^{-9} $s\cdot g\cdot Mol^{-1}$ at all the temperatures. The treatment of kinetic data further reveals that the ongoing adsorption proceeds via film diffusion process and adsorption of the dye is taking place mainly on the external surface of the De-oiled Soya. The pre exponential constant (D_o) and activation energy (E_a) have been found as 3.02×10^{-14} and 32.85 kJ mol^{-1} respectively. Under the column studies various parameters like fractional capacity of column, mass flow rate, percentage saturation of column etc. have been evaluated and their values have been found as 0.9748, 0.044 mg/cm^2/min and 98%, respectively. The recovery of the dye from the exhausted column was made by eluting dilute NaOH solution and almost 94% of the dye recovery was achieved.

1. Introduction

Eosin Yellow, is an anionic dye having IUPAC name, 2-(2,4,5,6-Tetrabromo-6-oxido-3-oxido-3H xanthenes-9-yl) benzoate disodium salt. It is highly water soluble and belongs to the fluorescein class of dye. Due to its ability of strong absorption by red blood cells and red color, Eosine Yellow is widely used in gram staining of differentiate bacterial species [1]. Edible usage of the dye has been banned by the US authorities due to toxic effects [2].

The toxicological information of Eosin Yellow reveals that the dye Eosine Yellow may cause severe skin and eye irritation. A physical contact of the dye on the skin causes irritation with redness and pain [3]. On ingestion, it poses several adverse effects particularly on the vital organs like liver, kidney etc. [4]. A direct contact of the dye with the eye can cause permanent injury to the cornea by the destroying retinal ganglion cell, located near the inner surface of the retina [5]. It also damages DNA in gastrointestinal organs of living beings resulting thereby in several types of diseases in the human body [6]. Inhalation of the dye reduces the pulmonary gas exchange capacity of the lungs [7]. Its metabolites are also highly toxic and carcinogenic in nature [8].

Keeping the toxicity of the Eosin Yellow in view, it was considered worthwhile to develop an economic and fast method for its removal from wastewater. From several decades various methods have evolved in wastewater treatment such as electrochemical treatment [9], oxidation [10], ozonation [11], photochemical treatment [12] and froth flotation [13]. It is now well established that for the wastewater treatment, adsorption has several advantages over other methods [14]. Moreover, the ability of adsorption to remove toxic chemicals without producing any toxic byproducts, thereby keeping quality of water undisturbed, has also popularized the adsorption technique in comparison to electrochemical, biochemical or photochemical degradation processes. During the past few years, the focus of the research is to utilize cheap materials as potential adsorbents and the processes developed so far are based on exploring such types of solid waste products, which can prove economical and bring cost effectiveness [15–50]. Therefore employing adsorption process for the removal and recovery of the costly dye like Eosin Yellow is advantageous and necessary, while the cost reduction of the developed process can be done by selecting a suitable waste material as adsorbent.

In the present paper attempts have been made to develop a fast and economical method for the removal of Eosin Yellow using

* Corresponding author. Tel.: +91 9425025427; fax: +91 755 2670562.
E-mail address: aljymittal@gmail.com (A. Mittal).

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De-oiled Soya as adsorbent. De-oiled Soya is a waste material, which has been processed out from the Soya Oil industries. It is obtained as a bye product after extracting all possible nutrients of Soya beans. It is a porous and dry flaky material, with brownish white color. Its use as animal feed is banned nowadays due to the formation of anti-metabolites activities in their digestive systems [51,52]. India is one of the major producers of the soya bean crop and captivatingly many soyabean oil extraction mills are situated in our state.

2. Material & methods

The dye Eosin Yellow, also known as Eosin Y, Eosin Yellowish, Acid Red 87, C.I. 45380, Bromoeosine, Bromofluoresceic acid and D&C Red No. 22, possesses molecular formula $C_{20}H_6Br_4Na_2O_5$ (molecular weight 691.88). It is procured from M/s Merck and used as obtained. Double distilled water was used for the preparation of 1×10^{-3} M stock solution of the dye and all further solutions were prepared by diluting the stock with distilled water. Adsorbent De-oiled Soya was a free gift from M/s Sanwaria Agro Oils Limited Bhopal, India. In order to adjust the pH of the solution dilute HCl and NaOH were used. All other chemicals used are of AR grade.

The microprocessor based pH meter model number HI 8424 (M/s Henna Instruments, Italy) was used to measure the pH of the solutions. The absorption studies were carried out using UV/Visible spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India). To measure various physical properties of De-oiled Soya, instruments like Mercury Porosimeter was used to determine porosity of the material, specific gravity bottles were employed to find out density and Quantasorb Model QS-7 surface area analyzer was used to measure surface area. To characterize De-oiled Soya, the IR spectrum was recorded on Infra-Red Spetrophotometer (HP FT-IR), Scanning Electron Microscope experiments were performed on Philips SEM 501 electron microscope, while X-ray measurements were carried out on Philips X-ray Diffractophotometer employing Nickel Filtered Cu-α-radiations.

3. Experimental

3.1. Material development

In order to enhance the adsorption ability of the De-oiled Soya the procured material is first subjected to the activation procedures. The dry flakes of De-oiled Soya were firstly groundd into very small granules, washed with double distilled water several times and then dried in an oven. To oxidize all undesired organic impurities, the dried material was then treated with hydrogen peroxide solution (30% w/v) at room temperature for about 24 h. The material thus obtained was further washed thoroughly several times by double distilled water and to expel moisture, it was once again kept into an electric oven at 100 °C for about 1 h. The activated adsorbent thus formed was then sieved to various mesh sizes such as 0.425–0.150 mm (36 BSS Mesh), 0.150–0.088 mm (100 BSS Mesh) and ≤ 0.088 mm (170 BSS Mesh) and finally stored separately in desiccators.

To determine the nature of De-oiled Soya, its weighted amount was added in 25 mL of distill water of pH = 7.0 and stirred thoroughly. The solution was kept undisturbed for 24 h in a 100 mL airtight measuring flask and then filtered to measure the pH. A decrease in the value of pH of the solution confirmed the acidic nature of the activated De-oiled Soya.

3.2. Adsorption studies

To carry out batch adsorption studies, in a 100 mL volumetric flask, 25 mL of the dye solution was taken at a fixed temperature and activated De-oiled Soya of a suitable mesh size was then added into it. The desired pH of the solution was now maintained by dilute HCl and/or dilute NaOH and the mixture was given intermittent shaking on a mechanical shaker. After about 24 h, when equilibrium is thought to be established, the solution was filtered using Whattman filter paper (No. 41) and the amount of dye uptake was monitored spectrophotometrically at the absorbance maximum of Eosin Yellow, viz. λ_{max} 516 nm. It is important to note that under batch studies, the effects of important parameters such as dye concentration, solution pH, sieve size and amount of the adsorbent material, solution temperature and contact time were observed.

3.3. Kinetic studies

In order to monitor the kinetics of the ongoing adsorption process, in a series of 100 mL airtight volumetric flasks, 25 mL of the dye solutions was taken in each and a suitable amount of the adsorbent of known mesh size was added into these. Flasks were taken in a water bath and agitated periodically on a mechanical shaker. These solutions were then filtered after a particular time interval and spectrophotometric analysis was carried out for the dye uptake.

3.4. Column studies

The bulk removal of the dye and its recovery was carried out through adsorption and desorption, respectively using column operations. To prepare the column a long tubular glass column of 30 cm length and 1 cm internal diameter was used. De-oiled Soya granules were dipped in double distilled water and kept overnight. Over the support of small amount of glass wool, slurry of De-oiled Soya was carefully fed in the column. In order to avoid air entrapment, the outlet of the column was kept open throughout the feeding. Once the homogeneous bed of the adsorbent is formed in the glass column, its outlet was closed. Now a dye solution of 1×10^{-4} M concentration was percolated at a flow rate of 0.5 mL/min and expelled dye solutions, each of 10 mL volume, were collected in test tubes to monitor the dye concentration by UV/Visible spectrophotometer. The continuous adsorption of the dye over the adsorbent surface ultimately exhausted the column bed and at this stage the feeding of the dye solution to the column was stopped. In order to retrieve the adsorbed material from exhausted adsorbent, dilute NaOH was percolated through the column bed and solution thus obtained was finally dried. When dye was drained out almost completely, the adsorbent bed of the column was properly washed with hot water and the column was made ready for the next cycle of operation.

4. Result and discussion

4.1. Characterization of adsorbent

The characterization of the activated De-oiled Soya was carried out by conventional chemical methods. It was found that the dry sample contains maximum profit percentage (about 48%), while proteins, moisture, fiber, SiO_2, P, and Ca were present 29.0, 11.0, 6.0, 2.0, 0.7, and 0.2%, respectively. Other physicochemical properties like, surface area, density, porosity and loss of ignition of dry activated De-oiled Soya were obtained as 728.6 $cm^2\cdot g^{-1}$, 0.5614 $g\cdot mL^{-1}$, 67% and 4.27%, respectively.

The Differential Thermogravimetry Analysis (DTA) curves of the activated De-oiled Soya exhibit its good thermal stability and negligible weight loss was accounted. SEM photographs ascertained that the particulates of activated De-oiled Soya are porous and almost spherical. The Infra-Red spectrum of the activated De-oiled Soya gave sharp absorption bands at 479, 779, 1113, and 3459 cm^{-1}, confirming thereby the presence of gorthite [4(FeO·OH)], Coesite [SiO_2], Corundum [2(α-Al_2O_3)], and Laumonite [4($CaAl_2Si_4O_{12}\cdot4H_2O$)], respectively.