Silkworm Pupa as a Novel Adsorbent for the Removal of Dyes

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1. Introduction

The natural water resources of the world are becoming increasingly polluted and are unable to meet increasing industrial demands[1]. Each particular process in textile industry can have its own environmental problems. Two solutions to the problems exist, i.e. clean technology or effluent treatment, in other words prevention or cure[2]. Textile industries consume large volumes of water and chemicals for wet processing of textiles[3]. Textile wet processing involves the use of a variety of chemicals comprising various classes of dyes and other chemicals, known as auxiliary chemicals[4]. The major environmental problem that arises from the use of colorants is the removal of dyes from effluent[5]. The problem is not only associated with the toxicity of the dyes released, also the colored effluent flowing through drains. The large quantity of the effluent from a dyeing unit and the extent of pollution in it can adversely affect aquatic life. Such waste streams need, therefore, desired treatment prior to their disposal which calls for the most appropriate treatment option[4]. Colour is usually noticeable at concentrations above 1 mg/1 of dyes and has been reported in effluent from textile manufacturing processes at concentrations exceeding 300 mg/l[6]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable. There are more than 100,000 commercially available dyes[3,7].Many dyes are difficult to decolorize due to their complex structure and synthetic origin. There are many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes[3]. Decolouration of textile dye effluent does not occur when treated aerobically by conventional municipal sewerage systems[3,6,8,9]. Therefore, it is necessary to find an effective method of wastewater treatment capable of removing colour and toxic organic compounds from textile effluents. These less or non-biodegradable compounds, called xenobiotics, can not be completely removed by biological treatment and wastewater contaminated with these substances must be treated by physical and chemical means[8]. Due to increasingly stringent environmental legislation, the textile industry in the world is seeking to develop effective wastewater remediation technologies, especially those that allow colour removal that is largely unaffected by conventional treatment systems. Despite the existence of a variety of chemical and physical treatment processes, bioremediation of textile effluent is still seen as an attractive solution due to its reputation as a low-cost, environmentally friendly, and publicly acceptable treatment technology[7]. The use of adsorption techniques offers much potential in the treatment of dye-containing effluents. Adsorption methods allow the dye to be dealt with on a solid substrate, which can be renewable resource. Rather than attempting to remove the dye and degrade it at the same time, adsorption offers the alternative of splitting up these two steps once the dye has been adsorbed onto the substrate. It is in a more treatable form. This fermented substrate then has the potential to be used as soil conditioner or fertilizer in the case of agriculture resource of adsorbent.Decolourisation is a result of two mechanisms: adsorption and ion exchange, and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time[3].Since cost is an important parameter in most developing countries efforts have been made to explore the possibility of using various low cost adsorbents for contaminant removal including dyes, heavy metals and organics and inorganic contaminants. These are either biodegradable, derived from plant or animal waste, or are industrial by products. Most of the adsorbents explored for decolorization studies are cheap, require little or no processing, are easily available and are biodegradable or easily disposed by incineration thereby providing energy[10]. The mechanism of dye adsorption on the adsorbent in colour removal processes involves the following three steps[10,11]: diffusion of dye molecules through the solution on to the surface of the adsorbents, adsorption of dye molecules on the surface of the materials through molecular interactions and diffusion of dye molecules from the surface into the interior of the adsorbent materials.

Adsorption isotherms are a useful quantitative tool when representing the adsorption capacity of an adsorbent for a given solute. However isotherms are obtained under equilibrium conditions, whereas in most adsorption treatment applications the retention time is too short for equilibrium to be attained. For this reason one must obtain information on the time dependence of adsorption processes by carrying out process-orientated kinetic studies[12].

In this work the use of silkworm pupa, which is the waste of silk spinning industry, as an adsorbent for dyes removal from their aqueous solution has been investigated. Because of amino acid nature of the pupa it is predicted that it could have a reasonable capability for dye adsorption. Adsorption study was carried out by assessment of two adsorption isotherms i.e. Langmuir, Freundlich. Parameters such as temperature, agitation time and pH have been investigated.

2. Materials and methods

Silkworm pupa was first powdered and washed with distilled water. This powder was used for adsorption studies after drying and sieving. The mesh size of adsorbent was between 50 and 100. Adsorption of basic blue 41 (a cationic dye from Ciba) was carried out in a batch process by varying dye concentration, pH of medium and temperature. The mixture, in a 100-ml conical flask, was stirred by a heater stirrer (Yellow line –MST) equipped with temperature controller. If necessary, the pH was adjusted by adding a few drops of dilute NaOH or H_2SO_4 and measured by 744 pH meter Metrohm before each experiment. The mixture was allowed to settle and was centrifuged by Rotana 460R. The dye concentration after adsorption process was determined with a spectrophotometer (Cintra 10 UV-Vis Spectrophotometer) in maximum wavelength of dye. To determine which isotherm can be fitted on these data, the linear form of Freundlich and Langmuir equations[13,14] (equation 1and 2 respectively) were applied and correlation coefficient of two lines were calculated.

$\frac{aC_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$ (1) and $\frac{x}{m} = kC_e^{\,n}$ (2)

Where: C_e is the concentration of adsorbate (mg/L) at equilibrium, q_e is amount of solute adsorbed at equilibrium, constant $Q_o$signifies the adsorption capacity, a and b is related to the energy of adsorption, k and n are Freundlich constants

3. Results and discussion

Experiments suggest that equilibrium could be reached in about 60 min. General adsorption isotherm of cationic dye by silk worm pupa is shown in Fig. 1. The best isotherm equation that can be fitted to the obtained data is Langmuir (Fig. 2) with correlation coefficient about (0.982). Adsorption capacity of silkworm pupa for basic blue 41 has been calculated about 190 mg/g. Fig. 3 shows that by increasing the initial dye concentration the amount of adsorbed dye by adsorbent will increase. In the region of applied concentrations this relation can be demonstrated well by a linear equation. The determining parameter for adsorption by silkworm pupa, according to its nature, is pH. As shown in Fig. 4 with the increasing pH values, the adsorption of dye on silkworm pupa tends to increase, which can be explained by the electrostatic interaction of dye cationic species with the negatively charged surface. The electrostatic attraction force of the dye compound with the adsorbent surface is likely to be raised when the pH value increases.

Fig. 5 shows that the removal of dye by adsorption on silkworm pupa increases by increasing the temperature of the solution from 20 to 50 ^{o}C indicating the process to be endothermic. This kind of temperature dependence of the amount of the dye adsorbed may reflect the increase in the case with which the dye penetrates into the adsorbent because of its larger diffusion coefficient.

The second-order kinetic model is expressed as[14]:

$t/q = 1/k_{ad2}\, q_e^2 + t/q_e$ (3)

where k_{ad2}(s g/mg) is the rate constant of second order adsorption.

The linear plot of t/qversus t(Fig. 6) shows a good agreement between experimental and calculated q_e values. The correlation coefficients for the second-order kinetic model are greater than 0.999 indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of basic blue 41 on silkworm pupa.

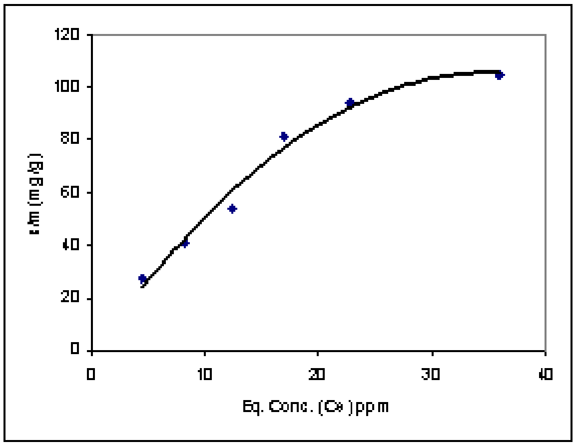

Fig. 1. General adsorption isotherm on silkworm pupa.

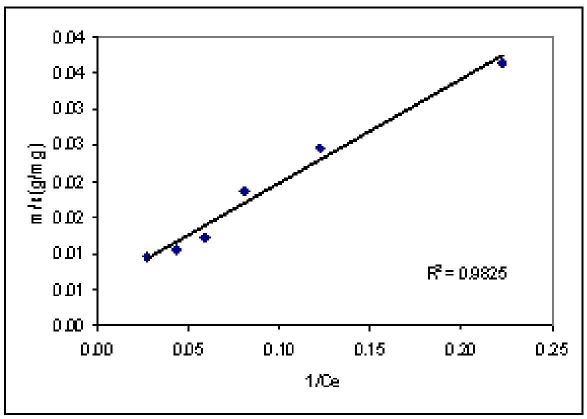

Fig. 2. Linear form of Langmuir adsorption isotherm.

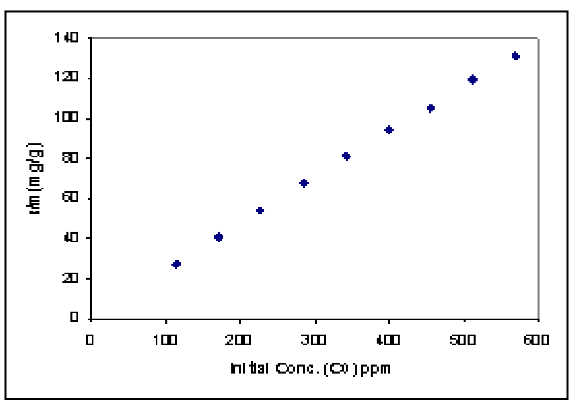

Fig. 3. Effect of initial dye concentration on the cationic dye removal by silkworm pupa.

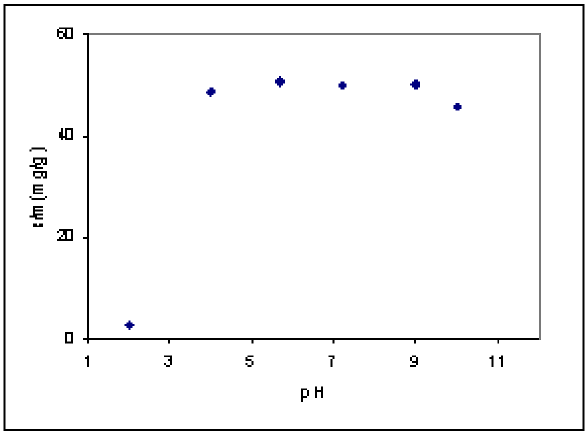

Fig. 4. Effect of pH on the cationic dye removal by silkworm pupa.

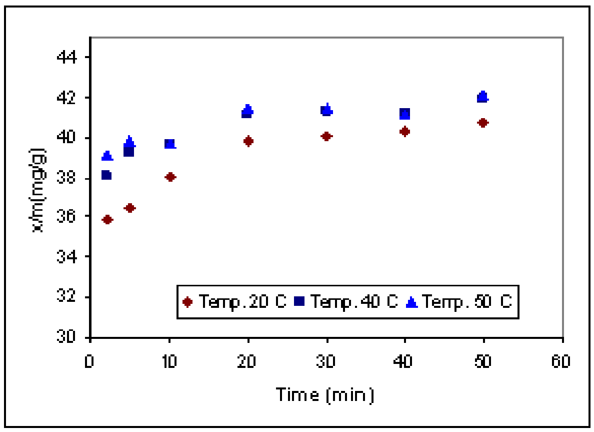

Fig. 5. Effect of temperature on the cationic dye removal by silkworm pupa.

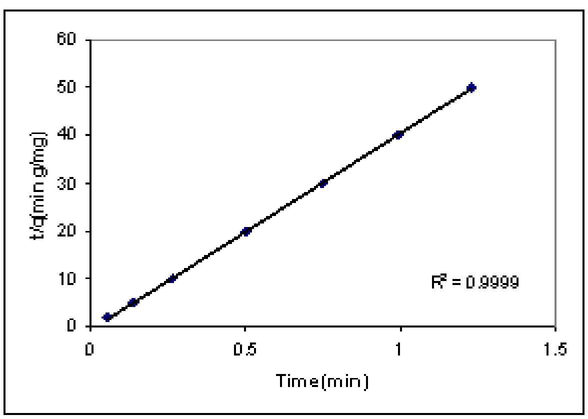

Fig. 6. Linear form of second-order kinetics for adsorption

of cationic dye on silk worm pupa.

4. Conclusion

In this study it has been found that silkworm pupa has a fairly good adsorption property for selected basic dye. Parameters such as pH, agitation time and temperature have been investigated. The most important factor for this adsorbent is pH of the solution.

5. Acknowledgement

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