REMOVAL OF DIRECT GREEN 26 DYEFROM AQUEOUS SOLUTIONS USING EGGSHELL

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Abstract - Biosorption of directgreen 26 dye(DG 26) onto eggshells as a new and potential biosorbent havebeen studied. Batch biosorption studies were conducted to evaluate the effect of various parameters suchas contact time, temperature, pH, initial dye concentration, and biosorbent dosage on theremoval of DG 26. Adsorption isotherm data were fitted to the Freundlich isotherm and the model parameters of the have been determined. The results showed that it took about 30 minutes for the process to reach the equilibrium state. The optimum temperature and pH for removal of DG 26 was 10 and 45°C, respectively. In addition, the effects of dye concentration and adsorbent dosage on the process were discussed. It was concluded that eggshell is potentially a good adsorbent for removal of DG 26 from wastewaters.

Keywords - Dye, Removal, Adsorbent, Eggshell.

I. INTRODUCTION

Dyes are used as coloring substances in plethora of industries, such as various textile industry applications, food, paper, carpets, rubbers, plastics and cosmetics [1–3]. The discharge of colored wastewater from these industrial plants into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand (COD) of the effluent, and also reducing light penetration, which has a derogatory effect on photosynthetic phenomena. From the aesthetic and health point of view, the presence of dyes (carcinogenic compounds in particular) in surface and underground waters is neither not safe, pleasant, nor welcomed [4].Many industries such as textile, feedstuffs, paper, leather, cosmetics, among others use dyes for colouring their final products and consequently produce large amounts of dye-containing effluents. The presence of dye containing waters can adversely affect the aquatic environment by impeding light penetration, precluding photosynthesis of aquatic flora [5]. Different processes for colour removal typically include physical, chemical and biological schemes. Some processes, such as electrochemical techniques and ion pair extraction, are relatively new for textile waste treatment, while others have been used in the industry for a long time. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances. Many works have been done on adsorption of dyes on different adsorbents [6-9]. Among various kinds of adsorbents, natural adsorbents are attractive, mostly due to their economic potential and availability [10-12]. The hen eggshell mainly consists of two regions: the mammillary matrix (i.e., eggshell membrane) consisting of interwoven protein fibers and spherical masses, and the spongy matrix (i.e., calcified eggshell) made of interstitial calcite or calcium carbonate crystals [13]. Notably, numerous funnel-shaped pore canals with submicron-scaled mouth are distributed on the surface of eggshell, forming connection passages between the shell membrane and the cuticle (a foamy layer of protein on the outer surface). The chemical composition (by weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%). The by-product eggshell weighs approximately 10% of the total mass (ca. 60 g) of hen egg, representing a significant waste from the egg-derived products processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment. However, the waste management was not a desirable practice in view of the environmental odor from biodegradation. Because of its high nutrition contents such as calcium, magnesium and phosphorus, the utilization of this food processing by-product was usually reused as a fertilizer, soil conditioner or an additive for animal feed. Due to its intrinsic pore structure in the calcifiedeggshell and the amount in abundance, it is thus feasible to grind the eggshell agrowaste in the preparation of fine powders, which might pavethe way for available materials such as porous adsorbents.

In the present work, the efficiency of broken particles of egg shell for removal of green 26 dye was experimentally investigated.

II. MATERIALS AND METHODS

The direct green 26 dye (DG26) was obtained from MERK (Germany). It is particularly suitable for dying of paper, leather, and textile. The chemical structure the dye is given in Fig. 1. The eggshells of chickens used in this study were collected from some kitchens. They were repeatedly washed several times with tap water followed by distilled water and then

left in open air for several days. Eggshells were crushed to a size of about 5 mm. No more treatments were done on the biosorbent. The resulting material was stored in a glass bottle for further use without any pretreatment.

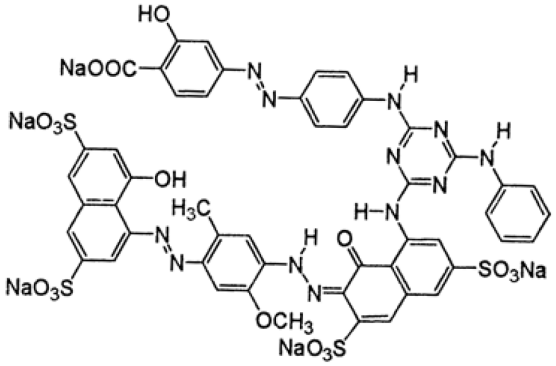

Fig.1. Chemical structure of DG 26

The experiments of biosorption kinetics were carried out to establish the influence of several parameters (contact time, temperature, initial dye concentration and pH) using a magnetic stirrer. All of the dye solution was prepared with distilled water. In the biosorption experiments, a certain amount of biosorbent was mixed with 100 ml of aqueous solution at the desired dye concentrations. 3 mL samples were drawn at suitable time intervals from the magnetic stirrer. The samples were then centrifuge 3 minutes at 2000 rpm and the concentration of the supernatant solution were analysed using a UV-Visiblespectrophotometer.The absorbance spectrum curve showed that the λmax of DG 26 was 625 nm. The concentration of dye was measured at this λmax with the calibration curve which was prepared by the use of the standard solutions of DG 26 (fig. 2).

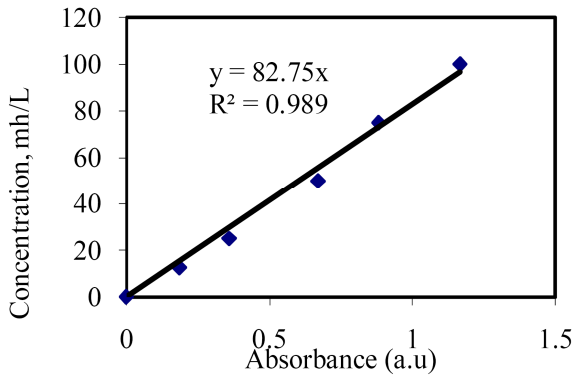

Fig2. Calibration curve for DG 26

IV. RESULTS AND DISCUSSION

The adsorption experiments were carried out in various operating conditions in order to findthe effects of adsorption time, temperature, initial dye concentration, adsorbent dosage and pH on the removal efficiency.

The effect of initial concentration and contact time on dye biosorption was examined at four concentration levels (12.5, 25, 50 and 100 mg/L). The results are plotted in fig. 3. As can be seen from this figure, the removal efficiency of DG 26 onto eggshells by biosorption is rapid initially and then slows down gradually until a state of equilibrium. This is probably due to initially a large number of vacant surface sites are available for biosorption, while progressively fewer remaining sites become increasingly difficult to occupy due to the existence of repulsive forces between the solute molecules of the solid and bulk phases.

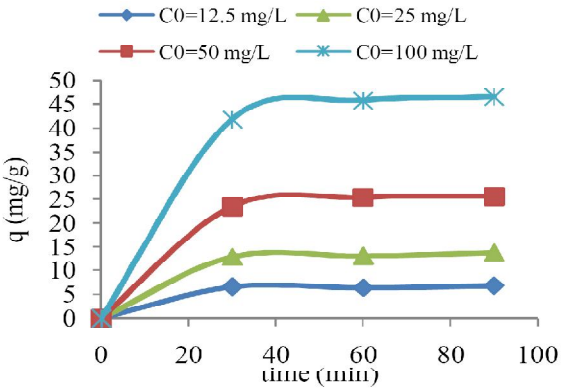

Fig.3. Effect of time and initial dye concentration on dye removal

In addition, fig. 3 shows that the equilibrium was reached in about 30 min. The removal of the dye was dependent on the initial concentration, so that the amount of adsorbed dye (q) increased from 7 to 47 mg/g with increasing of the initial dye concentration from 12.5 to 100 mg/L. It is because a higher initial concentration provides larger driving force to overcome resistances for diffusion of the dye between the aqueous and solid phases, thus increasing the uptake. In addition, increasing the initial dye concentration increases the number of collisions between dye ions and the surface area of adsorbent, which enhances the biosorption process.

The variation in the adsorption of the dyes was studied in the pH range of 3–11, and the results are shown in Fig. 4. It is observed that removal efficiency increasesslightly from 50% to 69% for an increase in pH from 3 to 10 and decreases quickly from 69% to 18% when pH increases from 10 to 11.

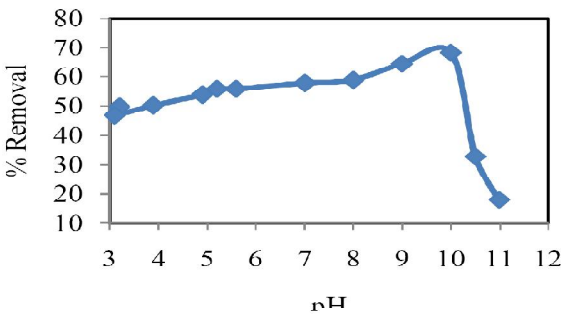

Fig. 4. Effect of pH on removal efficiency of DG 26 on eggshell

Therefore pH between 9 and 10 can be considered as the optimum pH for this process.
The effect of CES dose (varying from 1.0 to 6.0 g/L) on the % dye removal is presented in Fig. 5.

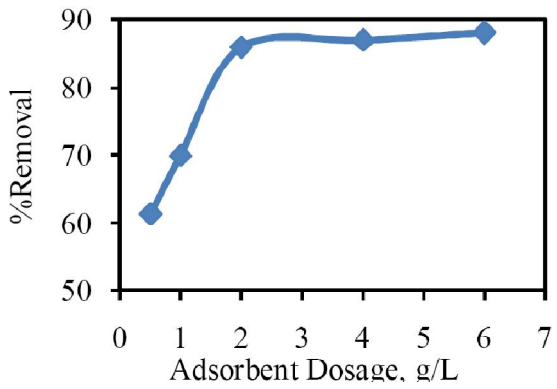

Fig. 5. Effect of biosorbent dose on the dye removal

As seen in Fig. 5, the removal percentage of DG 26 increased from 61% to 88% for increase of biosorbent dosage from 0.5 to 2 g/L. A more increase in the adsorbent dosage has few effects on enhancing the removal efficiency. Consequently, 2 g/L was used as optimal amount for further experiments.
Temperature is another factor that can influence the efficacy of adsorption process. In this research the effect of temperature on DG 26 adsorption within eggshells was studied (Fig. 6). This figure interprets that increasing of temperature from 7 to 45º C leads to elevation of removal efficiency of dye from 56% to 85%. However, more increase in the temperature causes the removal efficiency to descend. Therefore, 45°C can be considered as the optimum temperature for this process.
Biosorptionisotherms, describe how pollutants interact with biosorbentmaterials and are very important for optimization of biosorptionsystem. Equilibrium relationships between biosorbent and sorbateare described by biosorption isotherms, usually the ratio betweenthe quantity adsorbed and that remaining in the solution at a fixedtemperature at equilibrium.

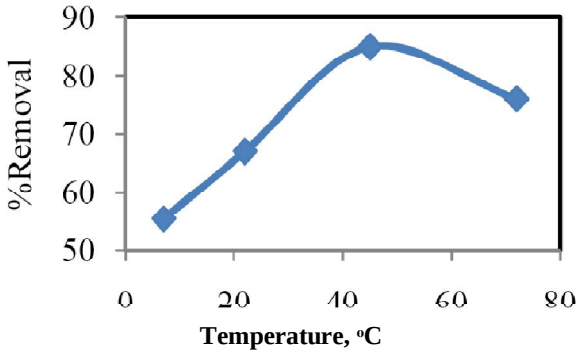

Fig. 6. Effect of temperature on the dye removal

There are several isotherm models available for analyzingexperimental data and for describing the equilibrium of biosorption.The empirical Freundlich equation was given as follows:

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \qquad (1)$$

where$K_f$and n are constants indicating adsorption capacity and intensity, respectively.Evaluation of the experimental data by Freundlich model is shown in fig.7. According to this figure, the model well fitted the experimental data and Kf and n are 1.2 L mg-1 and 1.3, respectively.

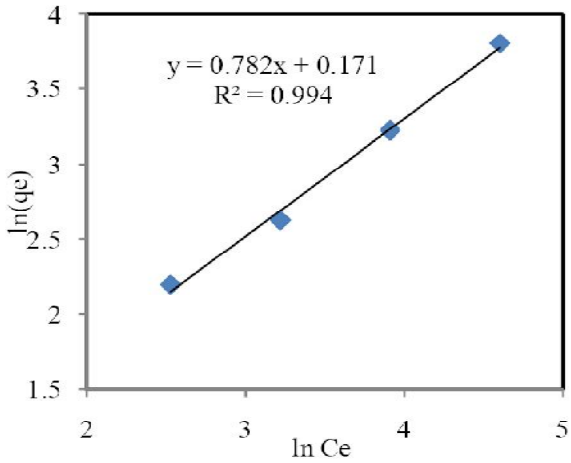

Fig.7. Evaluating the Freundlich isotherm

CONCLUSIONS

Removal of DG 26 on eggshell as an economic biosorbent was investigated. The results showed that the equilibrium state is gained after about 30 minutes. There is an optimum temperature of about 45°C and the range of 9 to 10 is the best for pH of the solution to reach the maximum removal of the dye. It can be concluded that eggshell is potentially a good chose for biosorption of DG 26.

ACKNOWLEDGMENTS

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