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Investigation on adsorption of dye (Reactive Red 35) on Egg shell powder

A.Babuponnusami¹*, S.Velmurugan²

¹Department of Chemical Engineering, VIT University, Vellore, Tamilnadu, India. ²Department of Chemical Engineering, Adhiparasakthi Engineering College, Melmaruvathur, India.

Abstract : Inexpensive and eco-friendly biosorbent Egg Shell Powder (ESP) has been successfully utilized for the removal of dye from aqueous solution. Reactive Red 35(RR 35)was used as model dye. The effects of initial dye concentration, adsorbent dose, adsorbent size and pH on adsorption capacity were investigated. The results indicate that the adsorption process is highly pH –dependant and the optimum pH for dye removal are3. The percentage removal of dye is inversely proportional to increase in initial dye concentration and directly proportional to adsorbent dosage. Smaller adsorbent particles add to increase the percentage removal of dye. The equilibrium data fitted well with the Langmuir model (R²= 0.995) and adsorption kinetics followed the pseudo-second order equation (R²= 0.99). The maximum adsorption capacity of RR 35 was calculated from Langmuir isotherm model and found to be 41.85 mg g⁻¹. From these results ESP can be employed as a low cost alternative adsorbent compared to other commercial adsorbents on the removal of dyes from wastewater.

Keywords : Adsorption, Reactive red 35, Dye, Egg Shell Powder, Adsorption Isotherm.

Introduction

Environmental problems due to industrialization and urbanization are become more frequent and complexin recent decades^{1, 2}.Rapid development in textile industries during recent years has led to the discharge of unprecedented amount of wastewater containing synthetic dyes. This waste water pollutes the natural environment and causes harm to human and other living organisms³. A very small amount of synthetic dye in water is highly visible and affects aquatic life and food webs due to the carcinogenic and mutagenic effects^{4,5}.

The increase in use of cellulosic fibres in textile industries requires large quantities of reactive dyes. This is due to the technical and economical limitations of other dyes used for these fibres ^{6,7}.

Synthetic dyes are difficult to biodegrade due to their complex aromatic structures, which provide physico-chemical, thermal and optical stability ⁸. Hence, it is imperative that a suitable treatment method should bedevised. In recent years, many methods including coagulation and flocculation ⁹, reverse osmosis ¹⁰, chemical oxidation¹¹biological treatments¹², photo degradation ¹³ and adsorption ¹⁴have been developed for treating textile wastewater.

Among various treatment technologies, adsorption technique is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents. Activated carbon is the most popular adsorbent for removal of dyestuffs from wastewater⁵. However, adsorbent grade carbon is cost prohibitive and both regeneration and disposal of the used carbon often very difficult. Therefore, there is a growing need to find locally available, low cost and effective materials for the removal of dyes.

In recent years, numerous low cost natural materials such as phyrophyllite¹⁵, rice husk¹⁶, montmorillonite¹⁷, activated carbon prepared from coir pith¹⁸, bagasse¹⁹, fungi²⁰, soil²¹, claymineral^{22,23}, fruit shell²⁴, water hyacinth root²⁵, and other natural materials from agricultural wastes²⁶⁻³² have been used and investigated for removal of various dyes from aqueous solution.

Meanwhile Hens' eggs are used in enormous numbers by food manufacturers and restaurants and the shells are discarded as waste. Many investigations have been conducted to explore useful applications for eggshells³³. Such research has shown that eggshells may be used as a fertiliser and a feed additive for livestock and it appears to be able to effectively adsorb certain heavy metals and organic compounds^{34,35}. The porous nature of eggshell makes it an attractive material to employ as an adsorbent. Each eggshell has been estimated to contain7000-17000 pores^{34,36}.

In this present work, Hen's egg shell powder (ESP) (a waste material) is used as an adsorbent for the treatment of Reactive Red 35containing aqueous solution. The effects of initial dye concentration, adsorbent dose, adsorbent size and pH on the adsorption of RR 35 were investigated.

Materials and Methods

Adsorbate

Commercial grade Reactive Red35 (CAS no.12226-12-9) is an azo dye with a molecular formula $C_{12}H_{18}N_3Na_3O_{14}S_4$ and molecular weight of 732.94 g/mol and was purchased from Aldrich. The maximum absorption wavelength of this dye is 530 nm. The structure of RR35 is shown in Figure 1.

Preparation of Biosorbent

Egg shells were collected from local food manufacturers and college canteen. The shells were then washed with distilled water followed by solar dried and ground into powder by using ball mill. The powdered egg shells were sieved to obtain particles of various size ranges and dried at 105° C in an oven for 2 h. The particle size of 105μ m, 149μ m, 210μ m and 354μ m were taken for adsorption studies. The egg shell powder was stored in air tight container for further use. No other chemical treatments were used prior to adsorption experiments.

Characterization of ESP

The surface area of ESP was determined using N_2 adsorption techniques (Micromeritics ASAP 2020 V3.00 H). The surface functional groups of ESP was detected by Fourier transform infrared (FTIR) spectroscope (FT-IR-2000, PerkinElmer one). In this analysis, aliquots of the sample were diluted and mixed with KBr to produce KBr pellets and then vacuum pressed. Absorbance spectra were recorded from 4000 to 400cm^{-1} with 16cm⁻¹ resolution.

Biosorption Experiment

Effect of pH

The effect of pH on amount of color removal was analysed over a pH range of 2-8. The pH was adjusted using 0.1N NaOH and 0.1N H_2SO_4 solutions and measured by a pH meter (Make: ELICO). In this study, experiments were carried out in 1000 mL of dye solution with 250 mg/L of initial dye concentration, 20g/L of ESP (105 µm in size) at room temperature of 30°C. Agitation was carried out for 2 h which is more than sufficient to reach equilibrium at constant agitation of 200 rpm. The aliquots were withdrawn at regular time interval and centrifuged immediately to separate adsorbent particles. Concentrations of dye solution was

determined by measuring the absorbance of the solution at the characteristics wavelength (λ max =530) of RR 35 using UV-vis spectrophotometer (Make: Sysytronics) by using calibration curve.

Biosorbent dosage and size

The effect of ESP concentration on the amount of color adsorbed was studied by adding various quantities (4, 8, 12, 16, 20, 24 and 28 g/L) of biosorbent in 1000 ml of dye solution of initial dye concentration 250 mg/L. All the experiments were carried out at 30°C, pH of 3, and 200 rpm for 1.5 h. The effect of biosorbent size (105, 149, 210 and 354 μ m) on dye removal is studied at the same condition.

Biosorption Equilibrium

The equilibrium experiments were carried out at 200 rpm by adding 20 g/L (105 μ m in size) of ESP to 1000ml of dye solution. The dye concentration was varied from 50-350 mg/L and all the experiments were performed in triplicates. The amount of RR 35 adsorbed per gram of ESP (q_e) as obtained using the following expression:

$$q_{\varrho} = \frac{(C_i - C_{\varrho})V}{1000M} \tag{1}$$

Where, C_i and C_e are the initial and equilibrium concentrations (mg/L)of RR35 solution respectively; q_e is the equilibrium uptake value (mg/g), V is the sample volume of the solution (L) and M (g)is the dry weight of the adsorbent. The percentage removal of the dye is given by

$$\Re Removal = 100 * \frac{(C_i - C_e)}{C_i}$$
⁽²⁾

Effect of Initial RR 35 Concentration

Experiments were carried out by mixing 20 g of ESP with 1000 ml of RR 35 solution of different initial dye concentration ranging from 50-350 mg/L. The studies were carried out at room using shaking incubator. After 2 h the samples were filtered ad analysed for residual RR 35. All experiments were carried out in triplicate under identical conditions and mean values are presented. The error obtained was 2.0 -4.5 %.

Results and Discussion

Characterization of Biosorbent

The specific surface area of the Egg Shell Powder (ESP) was studied by N_2 adsorption at 77K in which the sample was out gassed at 200°C for 12 h and found to be 2.12 m²/g.

The surface functional groups on sorbent was studied by Fourier transformed infrared (FT-IR) spectroscopic analysis and results are shown in Figure 2. The absorption peak obtained at 712 cm⁻¹, 874 cm⁻¹, 1419 cm⁻¹ and 2517 cm⁻¹ are the characteristic peaks of CaCO₃ present in the ESP³⁷. The peak occurred around 1798 cm⁻¹, and 2980 cm⁻¹ correspond to C=O from carbonate ion(CO₃⁻²). The very strong band at 1419 cm⁻¹ is related to the carbonate C–O bonds and the broad band at 3315 cm⁻¹ corresponds to the moisture absorption on the surface of the pellet³⁷.

The changes in morphology of the sorbent before and after the desired process were observed using scanning electron microscopy (VEGA3 TESCAN) and Figure 3(a)shows the surface of the sorbent before use, which contains rough and irregular layers that will enable sorption. The sorbent with a majority of micropores adsorbs dye molecules more readily. The sorbent after adsorption is shown in Figure 3(b). From the figure it is observed that the surface of the sorbent was completely covered by thick layer of adsorbate. The micropores present on the surface (appeared in Figure 3(a)) were not seen since the micropores were occupied by sorbate molecules.

Effect of pH on Biosorption of RR 35 dye

Since the pH is having vital role in the adsorption processes, the adsorption of RR 35 on ESP has been taken under various pH conditions. Effect of pH on the removal ofRR35 is shown in Figure 4. For 250 mg/L dye concentration the percentage dye removal decreased from 84.7 to 53.3%, when the pH was increased from 2 to 8. It has been concluded that, under strong acidic condition the adsorption process is good. It is due to the sulfonic acid functional groups in the RR 35.At the pH range of 2-4 the removal process is more than 80%. At the pH of 3 more positive charge is developed in the surface of adsorbent. Thus, strong interaction is developed between the sulfonic acid functional groups and adsorbent. The decrease of RR 35 removal may be related to the formation of negative surface charges of powdered eggshell at higher pH. As pH of the system decreased below the pH of the adsorbent, the number of negatively charged adsorbent sites decreased and the positively charged surface sites increased, which favours the adsorption of anions (anionic dye) due to electrostatic forces attraction^{5, 33}. The results show that the dye removal decrease with increasing initial pH of the dye solution and maximum removal occurs at pH 3. Therefore pH 3 was used for adsorption studies.

Effect of adsorbent dose

Figure 5 shows the removal of RR35 by powdered egg shell at different adsorbent doses (4-28 g) for the initial dye concentrations of 250 mg/L at pH 3. From the figure it is clearly observed that the percentage removal of dye is directly proportional to the adsorbent dosage. The sorption rate increased from 52.3% to 82.6% at equilibrium as ESP dose was increased from 4 to 28 g/L. This may be due to the increase in surface area of the adsorbent at higher concentrations of adsorbent⁵. But the sorption capacity decreased with increase in biosorbent dosage. As the biosorbent dose was increased from 4 to 28 g the sorption capacity of ESp decreased from 32.68 mg/g to 7.3 mg/g. this may be due to overlapping of sorption sites as a result of overcrowding of biosorbent particles³⁸.

Effect of adsorbent particle size

The effect of adsorbent particle size on dye removal was studied using different particle sizes (105, 149, 210 and 354 μ m) by maintaining the pH, initial dye concentration and adsorbent dosage of 3, 250 mg/L and 20 g/L respectively. The experiments were conducted at room temperature and the results are shown in Figure 6. From the figure, it was observed that the decrease in adsorbent size increased the percentage dye removal. As the particle size decreased from 354 μ m to 105 μ m the percentage dye removal was increased from 58.3% to 77.9%. The relatively higher adsorption with smaller adsorbent particles is due to the increase in surface area with decrease in particle size³⁹.

Effect of Biosorption equilibrium.

Adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and at constant temperature. The equilibrium adsorption isotherm is very important to design the adsorption systems. The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption ⁵. And also it provides the panorama of the system under study, indicating how efficiently and economically an adsorbent used in the system. For solid-liquid systems, several isotherm equations are available. In this study Langmuir and Freundlich equations were considered for equilibrium study.

The Langmuir isotherm

The theoretical Langmuir sorption isotherm is based on the assumption that the adsorption occurs at specific homogeneous sites within the adsorbent. The maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The non-linear equation of Langmuir isotherm model is expressed as follows:

$$\mathbf{q}_{e} = \frac{\mathbf{q}_{m} \mathbf{b} \mathbf{C}_{e}}{\mathbf{1} + \mathbf{b} \cdot \mathbf{C}_{e}} \text{ (or)} \frac{C_{e}}{q_{e}} = \frac{\mathbf{1}}{q_{m}b} + \frac{C_{e}}{q_{m}}$$
(3)

where, Ce is the supernatant concentration at the equilibrium state of the system (mg/L), qm and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively⁴⁰. The experimental data were fitted with Langmuir isotherm (Figure 7) and the constant together with R^2 values is listed in Table 1.

The Freundlich isotherm

The Freundlich isotherm model is the earliest known relationship describing the adsorption process. The model applies toadsorption on heterogeneous surfaces with interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of thesorptional centres of an adsorbent. Empirical equation of Freundlich isotherm is expressed as follows:

$$q_{e} = K_{f} C_{e}^{\frac{1}{n}} (\text{or})^{\log q_{e}} = \log K_{f} + \frac{1}{n} \log \Box C_{e}$$

$$\tag{4}$$

Where K_f is the Freundlich constant (L/g) related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favourable physical process⁴¹. The experimental data were fitted with Freundlich equation (Figure 8) and the constant from the graph are shown in Table 1.

From the table it is evident that the correlation co-efficient (R^2) value for Langmuir isotherm model (R^2 =0.995) is higher than that (R^2 =0.897) of Freundlich isotherm model. Since the value of R^2 nearer to 1 indicates that the respective equation is fitted with experimental data accurately. And also it indicates homogeneous distribution of active sites on the ESP surface, since Langmuir equation assumes that the surface is homogeneous. The adsorption capacity of RR 35 on ESP was found to be 41.85 mg/g.

Biosorption Kinetics

Figure 9 shows the effect of contact time on removal rate of RR 35 by powdered eggshell. Experimental studies were carried out with varying initial dye concentrations ranging from 50 -350 mg/L using 20 g/L of adsorbent dose at pH 7.3. The percentage removal of dye increased with increase in agitation time and reached equilibrium after 90 min for the dye concentrations used in this study. The percentage removal of RR 35 at equilibrium was decreased from 88.6 % to 30.2 % as the dye concentration increased from 50 to 350 mg/L. This may be due to increase in the initial concentration of dye which provides an important driving force to overcome all resistances of the dye between the aqueous and solid phases^{42, 43}. At lower concentrations, all sorbate ions present in the sorption medium could interact with the binding sites, hence higher percentage removal was obtained. At higher concentrations, the percentage removal of the dye shows a decreasing trend due to the saturation of the sorption sites^{43, 44}.

In order to investigate the mechanism of adsorption and steps that govern the overall removal rate in the adsorption process, kinetic models have been used. The pseudo-first order, pseudo-second order and intra particle diffusion model were tested to fit the experimental data obtained for RR 35 uptake by ESP. The rate constant for the adsorption process were determined using the model equations.

The pseudo-first order kinetic model with respect to solid/liquid adsorption systemcanbe written as⁴⁵:

$$\log(\mathbf{q}_{e} - \mathbf{q}_{t}) = \log \mathbf{q}_{e} - \frac{\mathbf{k}_{1} \mathbf{t}}{2}.303$$
⁽⁵⁾

Where, $q_e(mg / g)$ refers to the amount of dye adsorbed at equilibrium, $q_t(mg / g)$ refers to amount of dye adsorbed at time 't', k_1 is rate constant for pseudo-first order adsorption. The value of pseudo first order rate constant, k_1 , has been evaluated from the slope of the linear plot of $\log(q_e - q_t)$ verses t as shown in Figure 10.

The kinetic data were further analyzed using Ho's pseudo-second order kinetics model⁴⁶. This model is based on the assumption that the sorption follows second-order chemisorption. It can be expressed as:

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$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{k}_{2} \mathrm{q}_{\mathrm{e}}^{2}} + \frac{\mathrm{t}}{\mathrm{q}_{\mathrm{e}}}$$

Where, k_2 is the rate constant of second order adsorption. Values of k_2 and q_e were calculated from the plots of t/q_t versus t in Figure 11.

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the experimental data were fitted to the Weber's intraparticle diffusion which is expressed as⁴⁷:

$$\mathbf{q}_{t} = \mathbf{k}_{id} \mathbf{t}^{\frac{1}{2}} + \mathbf{C}$$
⁽⁷⁾

Where, C is the intercept and k_{id} is the intraparticle diffusion rate constant, (mg/gmin^{1/2}), which can be evaluated from the slope of the linear plot of q_t versus $t^{(1/2)}$ as shown in Figure 12. The value of C gives the idea of boundary layer effect on adsorption process. The conditions to be satisfied that the adsorption process obeys intraparticle diffusion are that the plot should be linear and pass through the origin. The deviation of this plot from the linearity indicates that the rate controlling step should be film diffusion controlled. It was observed from the Figure 12 that the plots possess multi-linear portions (i.e., two steps were involved in the adsorption of RR 35 onto the ESP). The first line arportion is due to the film diffusion and the second linear portion is due to the intraparticle diffusion⁴⁸.

The kinetic parameters for three kinetic models and correlation co-efficient are shown in Table 2. From the table it is observed that the correlation co-efficient of second order kinetic model ($R^2 = 0.959$) is greater than that of first order kinetic model ($R^2 = 0.9233$) and intra particle diffusion model ($R^2 = 0.904$). From the kinetic study it was observed that The R^2 value is higher for second order kinetic model and the corresponding rate constant is found to be 1.685 x 10⁻³ g/mg min. This shows that the Pseudo second order kinetic mechanism is predominant and that the overall rate of dye adsorption process appears to be controlled by chemisorption process.

Conclusion

Egg Shell Powder(ESP) used in this investigation is easily, abundantly and locally available and expected to economically viable for removal of RR35 from aqueous solution. The adsorption is strongly dependent on initial concentration of dye, pH, adsorbent dosage, and contact time. The effect of pH of aqueous solution decreases the removal efficiency with the increase in pH due to the ionic effect. The % RR35 removal increases from 52.3 to 82.6% for an increase in adsorbent dose from 4 to 28 g/L because of the concentration gradient between RR35 in the solution and theRR35 in the surface of the ESP. The increase in initial dye concentration also enhances the interaction between RR35andESP which results in the decreased percentage of RR35 removal with the increase in initial concentration of RR35. In the effect of contact time, the percentage removal increases with time up to 90min and remains almost constant. The decrease in adsorbent size increased the percentage removal of RR35 from 58.3% by 354 μ m to 77.9% by 105 μ m size. Adsorption isotherms study shows that the adsorption of RR35 onto ESP follows the Langmuir model, and the maximum adsorption capacity was found to be 41.85mg g^{-1} . The suitability of the pseudo first order, pseudo second order and intra particle diffusion kinetic model for the sorption of RR35 onto ESP is also discussed. The pseudo second order kinetic model (R^2 =0.959) agrees very well with the dynamic behaviour of the adsorption process. The adsorbent (ESP) investigated in this study thus exhibited a high potential adsorbent for the removal of RR35 from aqueous solution.

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