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Adsorption of acidic dyes from aqueous solution on eggshell and its membrane: Kinetics and equilibrium studies

Monika*, Amita
Department of Biotechnology, Mata Gujri College, Fatehgarh Sahib-140406 Punjab, (INDIA)
E-mail : monika187@rediffmail.com

ABSTRACT

The adsorption of two synthetic acidic dyes from aqueous solution has been investigated on eggshell and its membrane. The influence of pH, contact time, adsorbent dosage, dye concentration, agitation speed, temperature & particle size of biosorbent on the biosorption has been investigated. The biosorptive capacities of the biosorbents were dependent on the pH of the dye solution, with pH 2 being the optimal one. Two common isotherm equations were applied to model the isotherms in the present study i.e. the Langmuir and the Freundlich models. It was observed that the Langmuir model yields a better fit than the Freundlich model in case of both the dyes, as reflected with the correlation coefficients (R^2) in the two cases. The adsorption capacities were found to be 4.054, 14.34, 78.67 mg/g for ES+M, ES, ESM respectively in case of Acid Blue MTR Dye & similarly 2317.66, 10.94, 115.5 mg/g respectively in case of Acid Yellow 5GN Dye.

KEYWORDS

Waste water;
Textile effluent;
Acid blue MTR dye;
Environment;
Adsorption.

INTRODUCTION

Increasing environmental pollution from industrial wastewater particularly in developing countries is of major concern. Waste water from manufacturing or chemical processes in industries contributes to water pollution. Many industries like dye, textile, paper and plastic industries use dyes in order to colour their products and also consume substantial volumes of water. As a result they generate a considerable amount of coloured wastewater. The presence of small amount of dyes (less than 1 ppm) is highly visible and undesirable. Dyes usually have synthetic origins and complex aromatic molecular structures[1]. According to their dissociation in an aqueous solution, dyes can be classified as follows: - anionic: acid, direct and reactive dyes, cationic: basic dyes and nonionic: disperse dyes[2]. Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them[3,4].

Over the last few decades, several methods have been devised for the treatment and removal of dyes e.g. adsorptive bubble separation techniques resulted in the efficient removal (99%) of Direct Blue from wastewater[5], photodecomposition of dyes under UV irradiation in the presence of trivalent iron-oxalato complexes was also reported[6]. Major drawbacks of these conventional methods are high sludge production, handling and disposal problems, high cost, technical con-

straints, etc. So biosorption/adsorption technology came to the foreground of scientific interest as a potential basis for the design of novel wastewater treatment processes.

Present study has been carried out for the decolourization of two synthetic dyes i.e. acid blue MTR and acid yellow 5GN dye from aqueous solution. Batch experiments were performed by using three types of low cost biosorbents prepared from eggshell. Three types of biosorbents prepared were i.e. eggshell with membrane (ES+M), eggshell without membrane (ES) and eggshell membrane (ESM). The present study reports their sorption potential through kinetics tests and sorption isotherms, in batch conditions. The experimental data of dyes adsorption equilibrium were fitted by either the Langmuir or Freundlich equations.

EXPERIMENTAL METHODS

Procurement of eggshells- Discarded eggshells were collected from local restaurants. This is the waste material which is of no cost and easily available from market as well as home.

Preparation of biosorbents- Three different types of biosorbents were prepared by taking eggshell as starting material

Eggshell with membrane (ES+M)

To prevent decomposition, eggshells were first washed in tap water, then boiled in distilled water, and finally dried at 105 °C in a hot air oven for 2 h. Then, it was grinded and stored for later use in adsorption studies.

Membrane-free eggshell (ES)

Eggshells were first washed in tap water and then boiled in distilled water. The membranes were separated from the wet eggshells by hand. The membrane free eggshells were then dried in hot air oven for 2 hrs. and then grinded using a blender.

Eggshell membrane (ESM)

Eggshells were first washed in tap water and then boiled in distilled water. The membranes were separated from the wet eggshells by hand. The membranes were then dried at 105 °C in a hot air oven for 2 h and then grinded.

Batch sorption experiments of synthetic dyes with the three types of biosorbents

The three types of biosorbents prepared were evaluated for decolourization efficiency by using synthetic dyes. Adsorption experiment was carried out in batch mode by using a conical flask (250 ml) in which the selected biosorbent was added for treatment of synthetic dyes as well as optimization of process parameters for removal of dyes.The dye solution was agitated on shaker.

Decolourization Assay- Absorbance units were converted to concentration by using standard curves. Percentage dye removal was determined by using the following formula :

$$\%\ \text{DYE REMOVAL} = \frac{\text{initial concentration of dye} - \text{final concentration of dye}}{\text{Initial concentration of dye}} \times 100$$

Optimization of process parameters to develop an effective treatment technology with the three types of eggshell based biosorbents

Various process parameters (pH, contact time, amount of biosorbent, concentration of dye, agitation speed, temperature, particle size) and their effect on decolourization activity of eggshell material was observed.

Sorption studies

Sorption kinetics

The initial solution dye concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of dyes. For dyes removal kinetics studies, adsorbent was contacted with dye solution in a flask agitated vigorously at constant room temperature (30-35°C) with varying pH and contact times. Their dye concentrations were determined with a UV-visible spectrophotometer. The dye uptake qe (mg dye/g adsorbent) was determined as follows:

$$qe = (Co - Ct) \times V/m$$

Where Co and Ct are the initial and time dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (g) in dry form.

Each experimental point was an average of two independent sorption tests. Duplicate tests showed that the standard deviation of the results was ± 5 %.

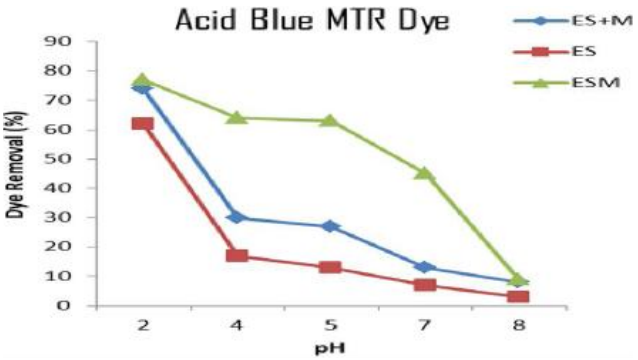
Sorption isotherms

The equilibrium isotherms were determined by contacting sorbent material with a range of different concentrations of dye solutions: 50-200 ppm. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 100 ml for definite optimized time intervals at room temperature. The equilibrium concentration of unbound dye was determined spectrophotometrically. The amount of dye adsorbed by the material was determined as the difference between the concentrations before and after adsorption.

RESULTS AND DISCUSSION

Optimization of various process parameters - To study the effect of process parameters on decolourization of synthetic dyes various operational parameters were considered like effect of pH, contact time, amount of biosorbent, concentration of dye, agitation speed, temperature, particle size. The results obtained from the study of various parameters on the biosorption of dyes are compiled as follows:

Effect of pH- To determine the effect of pH on decolourization of synthetic dyes with initial dye concentration of 100 ppm, the experiment was run with the adsorbent dose of 2g/100ml of synthetic dye in case of ES+M and ES and 0.2g/100ml in case of ESM for both the dyes at room temperature (30°C-35°C) under batch conditions for 3 hrs at a constant stirring speed of 150 rpm at different pH ranges (2,4,5,7,8). The filtered samples were then used to know the optical density and concentration of the sample. In both the dyes, it was observed that maximum decolourization (77%) was achieved at pH 2 in case of ES+M, ES and ESM. The adsorption capacity increases with decreasing the pH of the solution. Maximum adsorption of acidic dyes occurs at acidic pH-2. Dyes dissociated to polar groups ($R\text{-}SO_3^-$). ES and its membrane are comprised of various functional groups, such as amine, hydroxyl and carbonyl which could also be affected by the pH of the solutions. Therefore, at various pH, the electrostatic attraction as well as the structure of dye molecules and ES & ESM could play very important role in dye adsorption. At pH 2, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent due to the ionization of its functional groups and negative charged anionic dyes. At alkaline pH, the excess of OH^- ions destabilize the anionic dyes and compete with the dye anions (figure 1).



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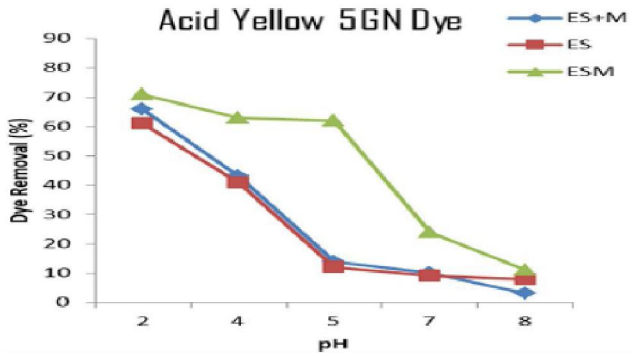

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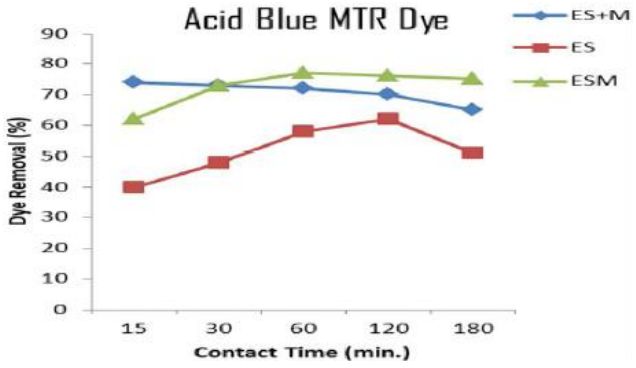
Figure 1 : Effect of pH on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of contact time

To investigate the effect of contact time on decolourization the synthetic dye was kept in contact with the biosorbent at the adsorbent dose of 2g/100ml of in case of ES+M and ES and 0.2g/100ml in case of ESM for both the dyes at room temperature (30°C-35°C) under batch conditions at a constant stirring speed of 150 rpm. After regular time intervals, the decolourization assay was done. In case of acid blue MTR dye, it was found that after 15 min in case of ES+M, 2 hr in case of ES and 1 hr in case of ESM, maximum decolourization was achieved. In case of Acid Yellow 5GN dye, it was found that after 1 hr in case of ES+M, ½ hr in case of ES and 1 hr in case of ESM, maximum decolourization (77%) was achieved. It was concluded from here that initially with increase in time, adsorption increases but after a specific time interval,

the equilibrium is achieved and then desorption of the dyes starts leading to decrease in adsorption of the dyes (figure 2).



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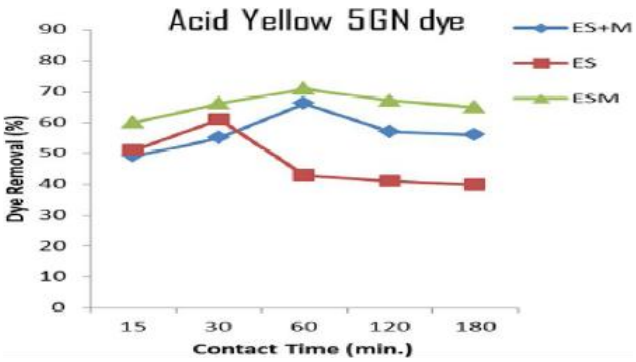

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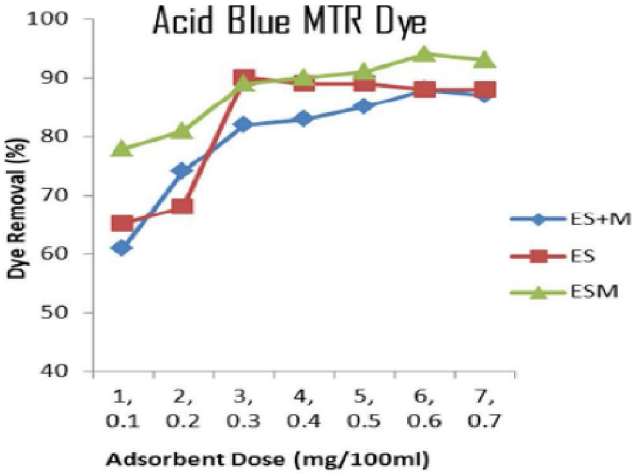
Figure 2 : Effect of contact time on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of adsorbent dose

The effect of adsorbent dose on decolourization was studied with initial dye concentration of 100 ppm, with various adsorbent doses under batch conditions at a constant stirring speed of 150 rpm. After a definite optimized time interval as optimized above i.e. 15 – 180 min., the treated samples were filtered and the decolourization assay was performed. In case of acid blue MTR dye, it was observed that maximum decolourization was achieved at dosage 6g in case of ES+M, 3g in case of ES and 0.6g in case of ESM.

In case of Acid Yellow 5GN dye, it was observed that maximum decolourization (94%) was achieved at dosage 3g in case of ES+M and ES and 0.4g in case of ESM. This suggests that as the adsorbent dose increase the extent of dye removal also increase but after a specific adsorbent dosage, the adsorption equilibrium is attained. The initial increase in adsorption with increase in adsorbent dosages can be attributed to greater surface area and availability of more biosorption sites (figure 3).



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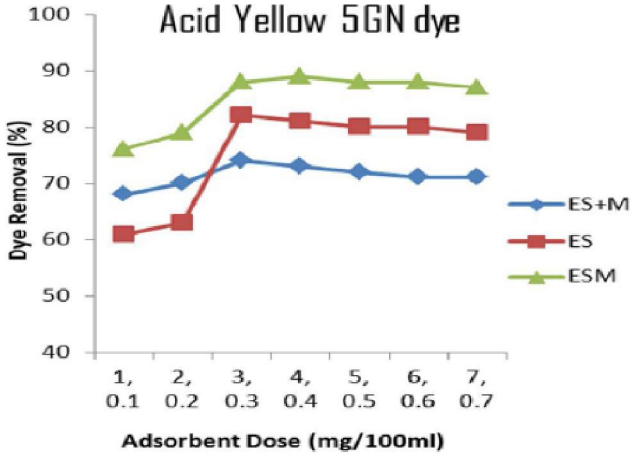

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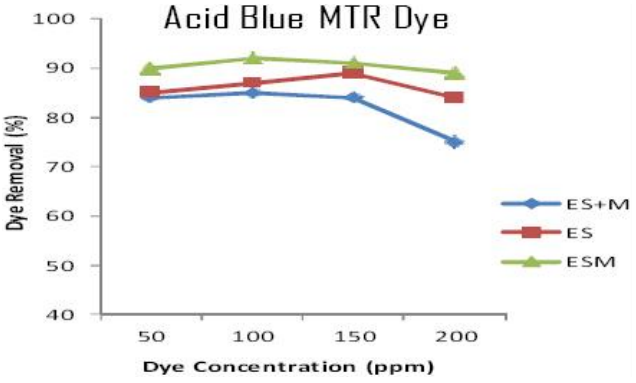
Figure 3 : Effect of adsorbent dosage on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of dye concentration

To observe the effect of varying dye concentrations on decolourization the synthetic dyes of various concentrations were kept in contact with the biosorbent at the adsorbent dosage of 6g/100ml of synthetic dye in case of ES+M,3g/100ml in case of ES and 0.6g/100ml in case of ESM in case of Acid Blue MTR dye and the adsorbent dosage of 3g/100ml of synthetic dye in case of ES+M and ES and 0.4g/100ml in case of ESM in case of Acid Yellow 5GN dye at room temperature (30°C-35°C) under batch conditions at a constant stirring. After a definite optimized time interval the decolourization assay was performed. In both the dyes,

it was found that maximum decolourization (92%) was achieved at dye concentration of 150 ppm in case of ES and 100 ppm in case of ESM. But in the case of ES+M, maximum decolourization was achieved at dye concentration of 100 ppm in case of Acid Blue MTR dye and 150 ppm in case of Acid Yellow 5GN dye. This indicates that the adsorption rate will increase with an increased initial dye concentration mainly due to the increase in the mass transfer from the concentration gradient, but after a certain concentration, the removal efficiency of adsorbent starts decreasing because of the limited adsorption sites available for the uptake of adsorbate (figure 4).



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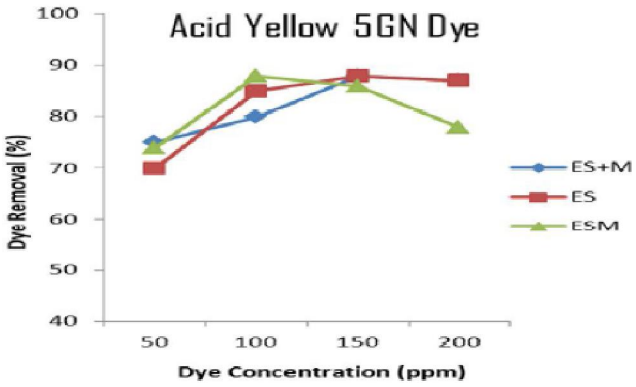

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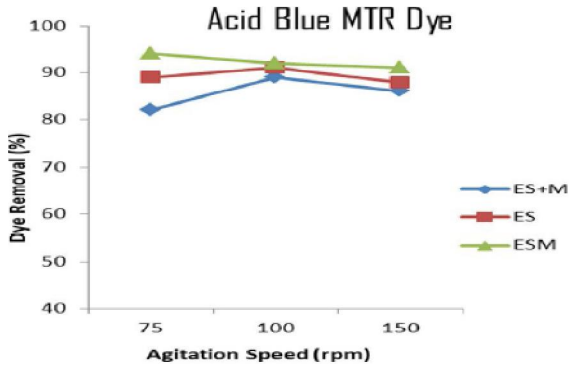
Figure 4 : Effect of dye concentration on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of agitation speed

To observe the effect of agitation speed on decolourization, synthetic dye with initial dye concentration of 100 ppm was mixed with adsorbent and kept on shaker at various agitation speeds i.e. 75 rpm, 100 rpm, 150 rpm. After a definite optimized time interval, the treated samples were filtered and the decolourization assay was performed. In both the dyes, maximum decolourization (94%) was achieved at 100 rpm in case of ES+M and ES and 75 rpm in case of ESM. It was observed that rate of removal of both the dyes was increased with increase in agitation speed in case of ES+M and ES because resistance to mass transfer is broken down with increasing agitation speed due to which more amount of colour penetrate into the adsorbent but beyond a certain agitation speed there was decrease in dye adsorption (figure 5).



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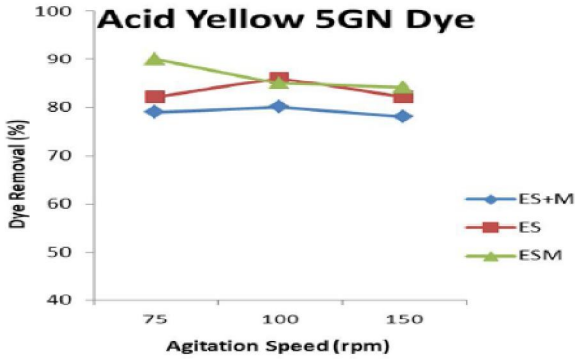

(b)

Figure 5 : Effect of agitation on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of temperature

The effect of temperature on decolourization was studied using synthetic dye with both dyes under batch conditions at a constant stirring speed of 150 rpm at various temperatures i.e. 25°C, 35°C and 40°C. After a definite optimized time i.e. 15-180 min., the treated samples were filtered decolourization assay was performed. In both the dyes, maximum decolourization (92%) was achieved at 35°C in case of ES+M, ES and ESM. Based on the results of the effect of temperature on the fitting adsorption capacity, the main mode

for adsorption of acid dyes onto ground eggshell was speculated to be strong dispersion forces and thus led to significant attraction between dye molecule and the ground eggshell particle, which should be an endothermic process, showing that the amount of dye adsorbed onto adsorbent increases with raising adsorption temperature up to 35°C (figure 6).

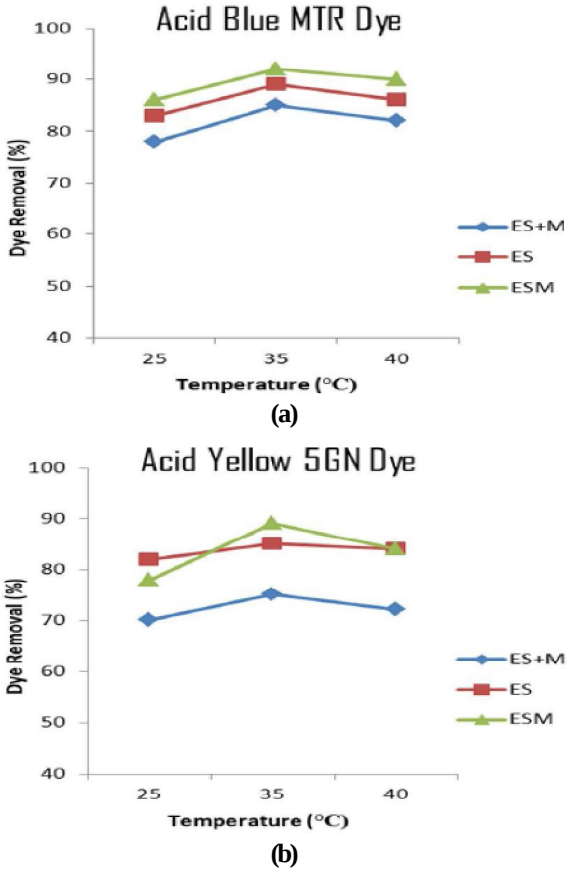

Figure 6 : Effect of temperature on % decolourization of (a) Acid Blue MTR Dye & (b)Acid Yellow 5GN dye by using ES+M, ES and ESM

Effect of particle size -The effect of particle size was investigated with initial dye concentration of 100 ppm with adsorbent of various size ranges (1.1mm-0.5mm, 0.5mm-0.18mm, ≤ 0.18mm) at the rate of adsorbent dosage of 6g/100ml of synthetic dye in case of ES+M, 3g/100ml in case of ES and 0.6g/100ml in case of ESM.

In case of Acid Blue MTR dye and the adsorbent dosage of 3g/100ml of synthetic dye in case of ES+M and ES and 0.4g/100ml in case of ESM in case of Acid Yellow 5GN dye at room temperature (30°C-35°C) under batch conditions. After a definite optimized time interval i.e. 15 min. to 180 min., the treated samples were filtered and decolourization assay was performed. In both the dyes, maximum decolourization (92%) was achieved at particle size range of ≤ 0.18mm in case of ES+M, ES and ESM. Results show that for both dye solutions, with decreasing the particle size, the adsorption is increasing to some extent. The rise in dye removal is the direct effect of the increasing surface area of the adsorbent by decreasing the particle size. All further studies were carried out choosing the particle size ≤ 0.18 (figure 7).

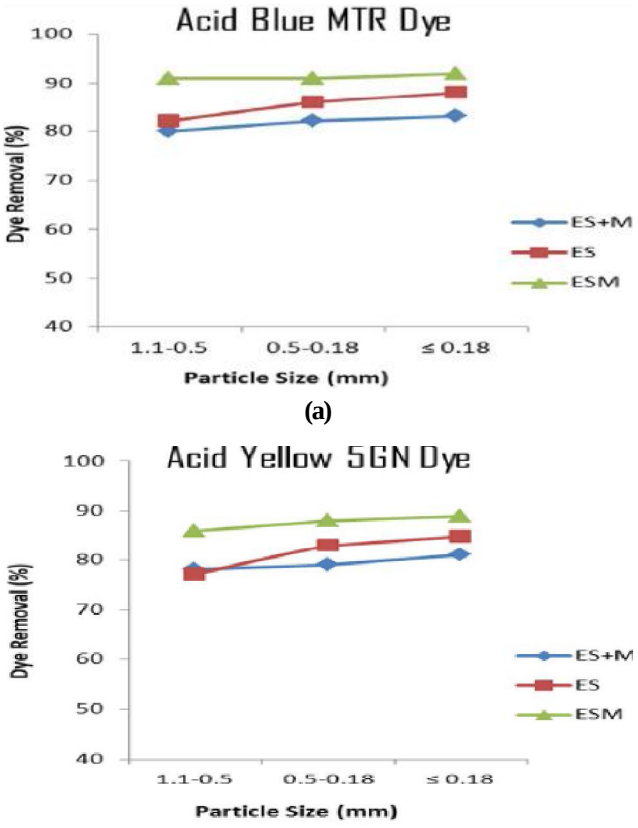

Figure 7 : Effect of particle size on % decolourization of (a) Acid Blue MTR Dye & (b) Acid Yellow 5GN dye by using ES+M, ES and ESM

Adsorption kinetics

In case of Acid Blue MTR dye- The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. As shown in figure 8, the kinetics of dye sorption was contact time dependent. Sorption increases with time and it remains constant after a contact time i.e. the equilibrium time. The response of the sorbent material

used is not similar with all the pHs (2, 4, 5, 7, 8). The equilibrium is achieved after 15 min. at pH 2 in case of eggshell with membrane, 2 hrs. at pH 2 in case of eggshell without membrane and 1 hr. at pH 2 in case of eggshell membrane.

In case of Acid Yellow 5GN dye - Figure 9 shows that change of dye adsorption with time goes by. As the contact time increases, dye uptake also goes up initially

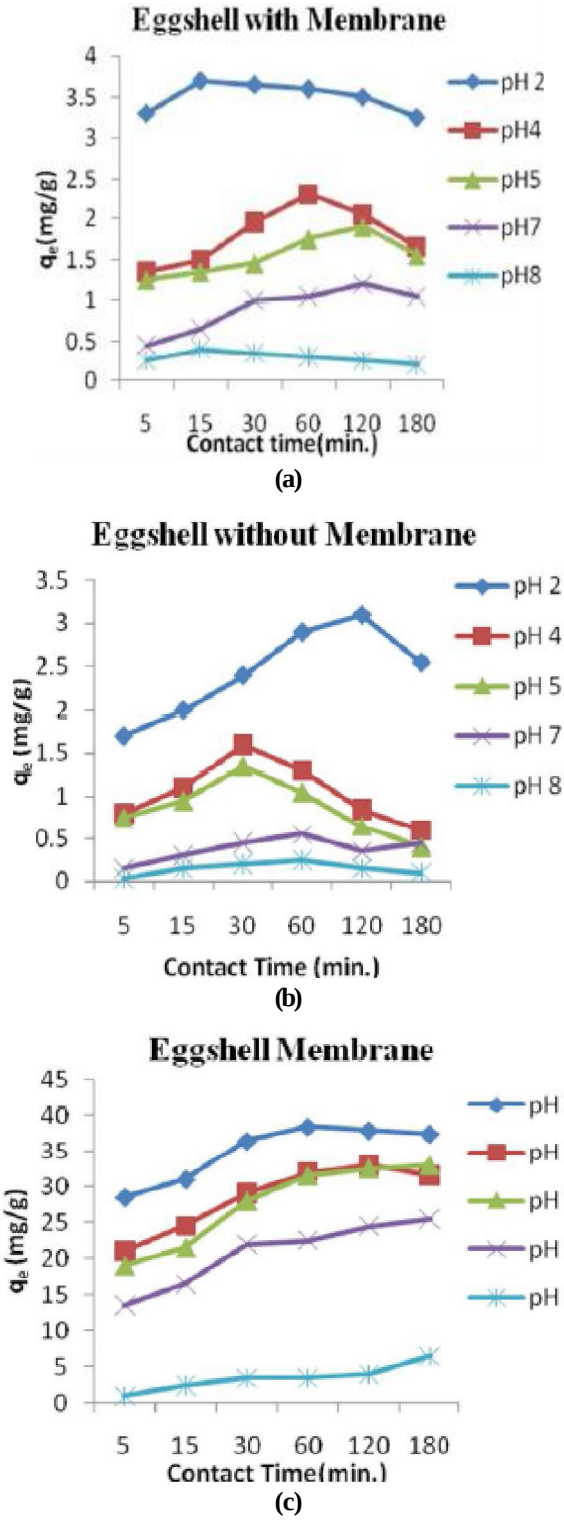

Figure 8 : Plot showing the adsorption kinetics of time vs. q_e (mg of dye adsorbed per gm of adsorbent) for Acid Blue MTR Dye by using (a) ES+M (b) ES (c) ESM

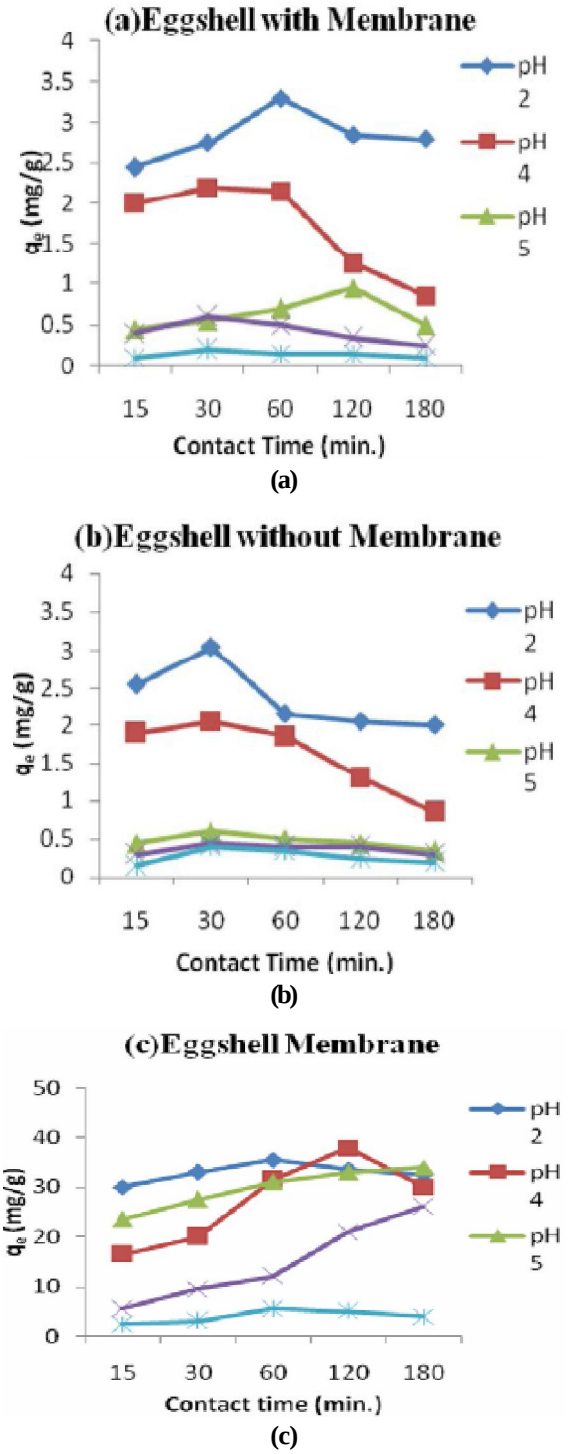

Figure 9 : Plot showing the adsorption kinetics of time vs. q_e (mg of dye adsorbed per gm of adsorbent) for Acid Yellow 5GN Dye by using (a) ES+M (b) ES (c) ESM

and then become almost stable, showing an attainment of equilibrium. The equilibrium was achieved after having been shaken for 1 hr. at pH 2 in case of eggshell with membrane, ½ hr. at pH 2 in case of eggshell without membrane and 1 hr. at pH 2 in case of eggshell membrane. The response of the sorbent material used is not similar with all the pHs (2, 4, 5, 7, 8). To assure that the true equilibrium is established, all the subsequent sorption experiments were carried out for about 3 hrs.

Adsorption isotherms

To facilitate the estimation of adsorption capacities at various liquid-phase concentrations of the two acidic dyes, the two well-known equilibrium adsorption isotherm models, Langmuir and Freundlich were employed as follows:

Langmuir: $q_e = q_m K_L C_e / (1+K_L C_e)$ [7]

Freundlich: $q_e = K_F C_e^{1/n}$ [8]

where q_e is the amount of dye adsorbed at equilibrium per g of sorbent (mg/g); C_e is the equilibrium concentration of dye in the solution (mg/L); q_m and K_L are the Langmuir model constants; K_F and 1/n are the Freundlich model constants. In the case of Langmuir isotherm, K_L is a direct measure for the intensity of the adsorption process (L/mg), and q_m is a constant related to the area occupied by a monolayer of absorbate, reflecting the adsorption capacity (mg/g). From a plot of 1/qe vs. $1/C_e$, q_m and K_L can be determined by its slope and intercept. In the case of Freundlich isotherm, K_F is a constant for the system, related to the bonding energy. K_F can be defined as adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbents for a unit equilibrium concentration (i.e., C_e = 1 mg/L). The slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity. A plot of ln q_e vs. ln C_e enables the empirical constants K_F and 1/n to be determined by the intercept and slope of the linear regression. TABLES 1 and 2 present the results of Langmuir and Freundlich isotherm fits by using the adsorption capacity data at 35 °C. Obviously, it can be seen that the Langmuir model yields a somewhat better fit than the Freundlich model, as reflected with correlation coefficients (R^2) of 0.945 vs. 0.229, 0.935 vs. 0.460 and 0.968 vs. 0.930 in case of acid blue MTR dye and correlation coefficients (R^2) of 0.866 vs. 0.371, 0.707 vs. 0.285 and 0.905 vs. 0.896 in case of acid yellow 5GN dye. From the results, it is concluded that both the dyes could be adsorbed largely and strongly on the ESM rather than ES or ES+M.

TABLE 1 : Langmuir parameters and freundlich parameters of different types of biosorbents prepared from eggshell for adsorption of acid blue MTR dye

Sorbent Type	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	1/n (-)	R^2
ES+M	4.054	28.13	0.945	3.5	0.341	0.229
ES	14.34	47.54	0.935	0.7	0.929	0.460
ESM	78.67	35.14	0.968	0.2	0.910	0.930

TABLE 2 : Langmuir parameters and Freundlich parameters of different types biosorbents prepared from eggshell for adsorption of acid yellow 5GN dye

Sorbent Type	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	1/n (-)	R^2
ES+M	17.66	83.78	0.866	0.8	0.990	0.371
ES	10.94	38.96	0.707	0.81	0.907	0.285
ESM	115.5	46.92	0.905	0.2	0.980	0.896

CONCLUSIONS

The present study concludes that the eggshell and its membrane could be employed as low cost adsorbent for removal of acidic dyes from waste water at low concentrations. Various process parameters (pH, contact time, amount of biosorbent, concentration of dye, agitation speed, temperature, particle size) and their effect on decolourization activity of eggshell material was observed. Two common isotherm equations were applied to model the isotherms in the present study i.e. the Langmuir and the Freundlich models. It was observed that the Langmuir model yields a better fit than the Freundlich model in case of both the dyes, as reflected with the correlation coefficients (R^2) in the two cases. Further investigation is required to study the reusability of biosorbent. An experiment can also be designed to test the removal of dye from textile effluents.

REFERENCES

[1] I.M.Banat, P.Nigam, D.Singh, R.Marchant; Microbial decolourization of textile-dye containing effluents: a review. Bioresour.Technol., **58(3)**, 217–227

(1996).

[2] G.Mishra, M.Tripathy; A critical review of the treatment for decolourization of textile effluent. Colourage, **40**, 35–38 **(1993)**.

[3] E.A.Clarke, R.Anliker; Organic dyes and pigments. In: Handbook of environmental chemistry, anthropogenic compounds, part A. New York: Springer-Verlag, **3**, 181–215 **(1980)**

[4] H.Zollinger; Azo dyes and pigments. Colour chemistry-synthesis, properties and applications of organic dyes and pigments. New York: VCH, 92-100 **(1987)**.

[5] J.Y.Horng, S.O.Huang; Removal of organic dye (direct blue) from synthetic wastewater by adsorptive bubble separation techniques. Environ.Sci. Technol., **27(6)**, 1169–1175 **(1993)**.

[6] D.Nansheng, W.Feng, L.Fan, L.Zan; Photodegradation of dyes in aqueous solutions containing Fe (III)-oxalato complexes. Chemosphere, **35(11)**, 2697–2706 **(1997)**.

[7] I.Langmuir; Adsorption of gases on plane surfaces of glass, mica and platinum. Journal of American of Chemistry Society, **40**, 1361-1403 **(1918)**.

[8] H.Freundlich; Colloid and capillary Chemistry, (Metheum, London), 883 **(1926)**.