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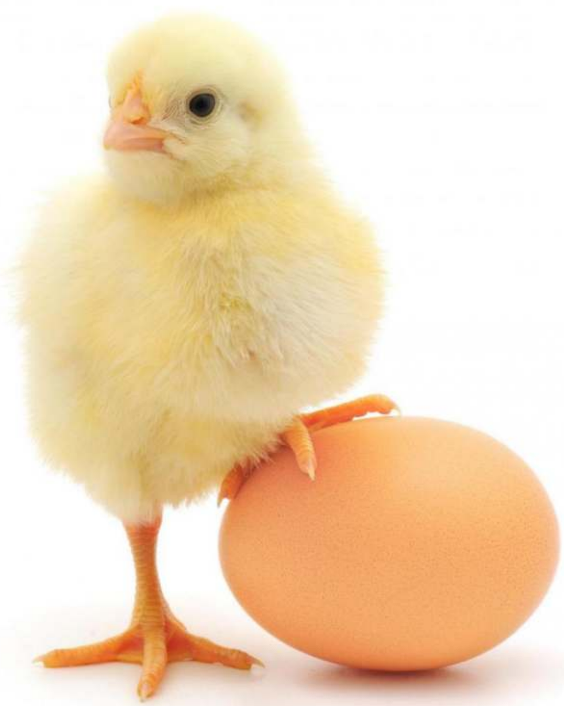

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Determination the Optimal Conditions of Methylene Blue Adsorption by the Chicken Egg Shell Membrane

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Abstract: The use of natural, cheaper and effective adsorbents like egg shell and its membrane and their mixture to bind three different types of dyes, methylene blue (cation), bromophenol blue (anion) and methyl orange (anion) from their aqueous solutions were investigated. The results indicate that the chicken Egg Shell Membrane (ESM) has the greater affinity for methylene blue than the other dyes. The egg shell membrane had a larger capacity to adsorb methylene blue (about 1.35 to 1.65 fold) as compared with Egg Shell (ES) and the mixture of Egg Shell and Membrane (ES+M). The optimum conditions for methylene blue adsorption including, particle size of the adsorbent (75, 125, 150, 212, 250 µm), pH (2, 4, 6, 8, 10), temperature (20, 40, 60, 80, 100)°C, contact time (5, 10, 15, 30, 60 min), adsorbent concentration (0.125, 0.25, 0.5, 0.75, 1.0 g/100 ml) and dye concentration (2, 4, 6, 8, 10 mg/100 ml) were investigated. The results showed that the highly percentages of dye removal by using egg shell membrane were observed with particle size of 250 µm, pH 10, at 80°C, for 30 min with 1.0 g/100 ml adsorbent and 2 mg/100 ml dye concentration.

Key words: Chicken egg shell membrane, optimum conditions, dye adsorption

INTRODUCTION

Dyes are chemical compounds have been used in many industries for coloration purposes such as, in food processing, textiles, papers, cosmetics and other industries (Sarioglu and Atay, 2006). The effluents from these industries are the main sources of environment dye pollution (Sarioglu and Atay, 2006). There are more than 100,000 commercial dyes with over 7 x 10^5 tons of dyes produced a annually and approximately 10% was discharged from textile and associated industries (Allen and Koumanova, 2005). Dyes are ionic, cationic and aromatic organic compounds, some of these dyes and their break down products may be toxic, mutagenic and carcinogenic for living organisms (Sarioglu and Atay, 2006; Ehrampoush *et al.*, 2011). Therefore, it is important to remove these pollutants from waste water before their final disposal (Ghani *et al.*, 2007).

Many physical, chemical and biological methods have been used to remove dyes from wastewater including, filtration, precipitation, coagulation, oxidation, ozone treatment and adsorption (Sarioglu and Atay, 2006; Allen and Koumanova, 2005; Pramanpol and Nitayapat, 2006). Adsorption technique is one of the most effective, low cost methods which used in recent years for dye removal from wastewaters to produce high quality water (Sarioglu and Atay, 2006). Among numerous types of adsorbents, different forms of activated carbon are commonly used for dye removal because it has a high capacity to adsorb organic compounds (Allen and Koumanova, 2005; Sarioglu and Atay, 2006). However this material is very expensive and its reactivation has several problems.

In recent years there are numerous researches focused on developing cheaper materials with more effective adsorption to remove dyes from wastes such as, fibres (Rasheed *et al.*, 2005), banana pitch (Namasivayam and Kanchana, 1993), biogas residual slurry (Namasivayam *et al.*, 2001; Namasivayam and Kavitha, 2002), chitosan (Juang *et al.*, 1996), hard wood (Asfour *et al.*, 1985), rice husk (Namasivayam and Kanchana, 1993; Mckay *et al.*, 1999), silica, bentonite, peat...... etc (Allen and Koumanova, 2005).

Eggs are used by enormous number of food manufactures and restaurants and the egg shell as a by-product represents approximately 11% of the whole egg weight is discard as waste. In Taion, for example, the annual generation of egg shell waste from the food processors was estimated to be over 1.3 x 10^4 tons from 1.7 x 10^9 chicken eggs. Many researches have been done to make use of egg shell in different applications such as, fertilizers, feed additive and adsorption heavy metals and organic compounds from waste water (Pramanpol and Nitayapat, 2006).

The chemical composition of egg shell (94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), as well as the porous nature of egg shell structure (7000-17000 pores) (William and Owen, 1995) makes it an attractive material to serve as an adsorbent agent. Furthermore, the inner eggs hell membrane has a good adsorption

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characteristics due to its composition (polysaccharides fibers and collagen like protein) (Allen and Koumanova, 2005), which containing substituting group sites such as hydroxyl, amine and sulfonic groups can react with dye (Allen and Koumanova, 2005).

The present work is studying the utilization of eggshell and its membrane as a dye discard material for three different types of dyes (Ionic, cationic and neutral dyes) to remove them from their aqueous solutions and determine the optimum conditions for the dye adsorption.

MATERIALS AND METHODS

Preparation of dye solutions: Three different types of analar dyes, methylene blue (cation), methyl orange (anion) and bromophenol blue (anion) were obtained by the assistance of BDH, Fluka and Merck chemical companies respectively. Dyes aqueous solution were prepared at concentration 10 mg/100 ml by using distilled water, the maximum absorbance wavelength (λ_{max}) for each dye was determined with absorbance spectrum ranged from 400-800 nm by using UV-Visible spectrophotometer. The standard curve of chosen dye (methylene blue) was prepared at concentration 1-10 mg/100 ml and detected (λ_{max}) to using it for measuring dye concentration in aqueous solution (Fig. 1).

Preparation of egg shell and its membrane: Egg shells with its membrane were collected, washed by distilled water and dried at ambient conditions. The membranes were separated from washed egg shell and the two samples were dried separately under ambient conditions. The egg shell, membrane and the mixture of dried egg shell and membrane were grounded separately by house mill to prepare powders with different particle sizes by using a standard sieves set (Fig. 2).

Adsorption of dyes by egg shell: Adsorption test was performed by mixing 1 g of each, egg shell membrane, egg shell and the mixture of egg shell and membrane of 250 µm particle size separately with 50 ml of 10 mg/100 ml concentration of methylene blue, methyl orange and bromophenol blue solutions (the pH was adjusted to 7). The mixtures were agitated at 35°C by using water bath shaker for 30 min then centrifuged at 10,000 rpm for 2 min to separate the adsorbent out of the liquid phase. The dye concentration, before and after the adsorption, for each solution was determined by measuring the absorbance at maximum wavelength (λ_{max}) by using UV-VIS spectrophotometer.

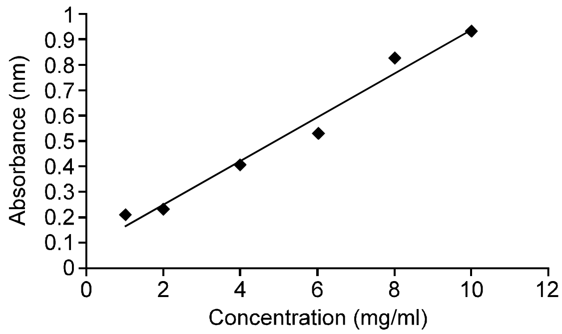

Fig. 1: The standard curve of methylene blue dye

Fig. 2: The dried powders of egg shell membrane, egg shell and the mixture of egg shell and membrane

The amount of adsorbed dye (Equ. 1) or the percentages of removal dye (Equ. 2) were calculated as follows:

$$qe = \frac{v}{m} x (C_0 - C) \quad (1)$$

$$E = \frac{C_0 - C}{C_0} x 100 \quad (2)$$

Where, C_0 and C are the concentrations of initial and remaining dye in solution (mg/L). qe, is the amount of dye on adsorbent (mg/g). v, the volume of dye solution (L). m, the mass of adsorbent (g) and E, the dye removal percentage (%).

The effect of particle size on dye adsorption: Adsorption test was carried out by mixing 1 g different particle sizes of egg shell membrane powder (75, 125, 150, 212 and 250 µm) with 50 ml of methylene blue solution (10 mg/100 ml of pH 7). The mixtures were agitated at 35°C for 30 min and centrifuged at 10,000

Table 1: The characteristics of the selected dyes

Dyes	Chemical formula	Molecular weight (g/mol)	Melting point	Type of dye	Boiling point	(λ_{max}) (nm)
Methylene blue	$C_{16}H_{18}N_3ScL$	319.85	100-110°C	Basic blue pH (9.4-14.0)	Decomposition	665
Methyl orange	$C_{14}H_{14}N_3NaO_3S$	327.33	>300°C	Acid-base indicator pH (3.1-4.4)	Decomposition	590
Bromophenol blue	$C_{19}H_{10}Br_4O_5S$	669.99	237°C with decomposes	Acid-base indicator pH (3-4.6)	Decomposition	465

rpm for 2 min. The dye concentration in each solution was determined by measuring the absorbance at 665 nm.

Effect of pH on dye adsorption: The pH of methylene blue solutions were adjusted to 2, 4, 6, 8 and 10 pH values. The solution were mixed with 1 g of egg shell membrane 250 µm particle size. The mixtures were agitated at 35°C for 30 min and centrifuged. The dye concentration was determined by measuring the absorbance of the solution at 665 nm.

Effect of temperature on dye adsorption: A solution of 1 g egg shell membrane (250 µm particle size) was added to 50 ml methylene blue solution (10 mg/ 100ml of pH 10) and agitated at different temperatures (20, 40, 60, 80, 100°C) for 30 min. After the centrifugation, the dye concentration was determined as above.

Effect of contact time on dye adsorption: The mixture of egg shell membrane (1 g of 250 µm) and methylene blue solution (10 mg/100 ml of pH 10) were agitated at 80°C for different time (5, 10, 15, 30, 60 min) and centrifuged. The dye concentration was determined as above.

Effect of adsorbent concentration on dye adsorption: Different amounts of egg shell membrane (0.125, 0.25, 0.5, 0.75, 1 g) were mixed with methylene blue solutions at concentration 10 mg/100 ml and pH 10. The mixture was agitated at 80°C for 30 min and then centrifuged. The dye concentration was determined as above.

The effect of dye concentration: One gram of egg shell membrane was mixed with 50 ml of methylene blue solution of different concentrations (2, 4, 6, 8, 10 mg/100 ml) at pH 10 and agitated at 80°C for 30 min. The mixtures were centrifuged and the dye concentration was determined as above.

RESULTS AND DISCUSSION

We have found that the maximum absorbance wave lengths (λ_{max}) of methylene blue, methyl orange and bromophenol blue dyes were 665, 465 and 590 nm respectively.

Figures 3, 4 and 5, showed that, the egg shell membrane has a high adsorption capacity to adsorb the selected dyes than the egg shell and the mixture of egg shell and membrane especially with the methylene blue (cationic dye) which was 3.3 mg/g, while it were 2.4 mg/g and 2 mg/g for egg shell and the mixture of egg shell and membrane respectively.

Similarly, the removal percentage of methylene blue from aqueous solution by egg shell membrane was high (66%) than the others (48.6% and 40% for egg shell and the mixture of egg shell and membrane

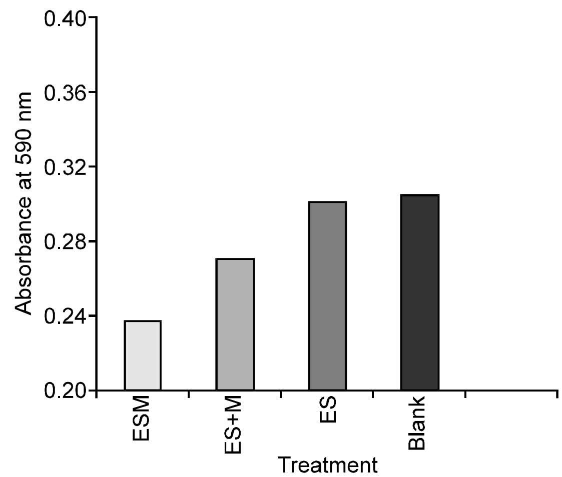

Fig. 3: Adsorption of bromophenol blue by Egg Shell (ES), the mixture of Egg Shell and Membrane (ES+M) and Egg Shell Membrane (ESM)

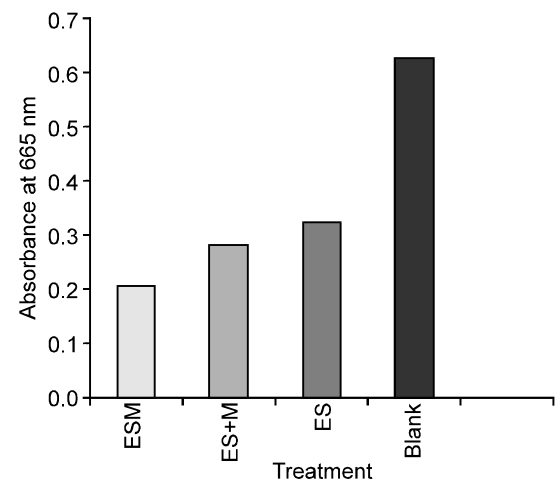

Fig. 4: Adsorption of methylene blue by Egg Shell (ES), the mixture of Egg Shell and Membrane (ES+M) and Egg Shell Membrane (ESM)

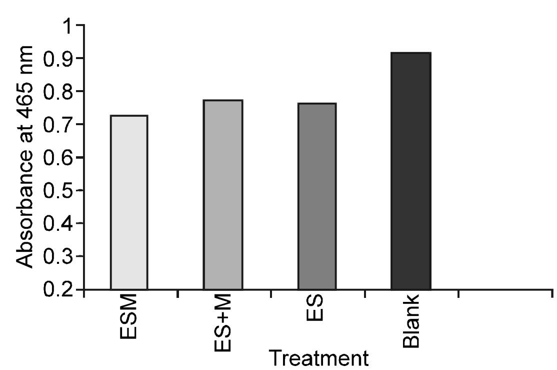

Fig. 5: Adsorption of methyl orange by Egg Shell (ES), the mixture of Egg Shell and Membrane (ES+M) and Egg Shell Membrane (ESM)

respectively). The results indicate that, the adsorption process is not only related to the properties of the pores within the egg shell structure, but also depending on the functional groups of the adsorbent surface (Allen and Koumanova, 2005).

The egg shell membrane is constructed of a network of fibrous proteins (95%) with small amount of polysaccharide (Parsons, 1982; Tsai *et al*., 2006). The membrane surface bears positively charged sites produced by the basic side chain of the amino acids (amines and amides) like arginine and lysine depending on the pH of the aqueous solution and this attribute to electrostatic attraction to oppositely charged species (Pramanpol and Nitayapat, 2006). Allen and Koumanova (2005) reported that, the membrane has good adsorption characteristics due to the availability of sites containing substituting groups such as hydroxyl, amine and sulfonic groups which can react with reactive dye. On the other hand, the porous nature of egg shell which contain about 7000-17000 pores makes it a good material to be used as adsorbent (William and Owen, 1995). There are many factors effecting the rate of adsorption including, dye structure, size or molecular weight, concentration and the charged groups (Allen and Koumanova, 2005). Methylene blue (cationic dye) was chosen as adsorbent to evaluate the optimum conditions of adsorb ability and effectiveness of egg shell membrane to remove this dye from aqueous solution.

Figure 6 shows the effect of adsorbent particle size on the ability to adsorb methylene blue from aqueous solution. The higher uptake of dye (4.73 mg/g) obtained by using 250 µm particle size diameter comparing with the other particle sizes (75, 125, 150, 212) µm which gave, 3.80, 4.26, 4.26, 4.47 mg/g respectively. As a result, the removal percentages of dye from the aqueous solution was 94.6%, 89.4%, 85.2%, 85.3% and 76% respectively. Although, the small size of egg shell membrane particles increases the surface area and in turn increasing dye adsorb ability, the results refer to a reduction in adsorption ability associated with decreasing in membrane particle size. These findings may be attributing to the use of excess time in milling process which can cause a structural changing due to a reduction of the crystallinity and affect the adsorption ability (Tsai *et al*., 2008). For example, the adsorption properties of egg shell powder mainly depend on its particle size, particle shape and porosity (Tsai *et al*., 2008).

The effect of pH on the adsorption process is illustrated in Fig. 7 that, the elevation of aqueous solution pH leads to increase the dye adsorption by egg shell membrane. As the pH value increased from 2 to 10, the dye adsorption increased from 3.6 to 4.6 mg/g, similarly, a higher removal percentages of dye from solution were observed, 73.3%, 86%, 88%, 90.6%, 93.3% at pH 2, 4, 6, 8, 10 respectively. These results can be attributed to the effect of the solution pH on the charge of reactive group within egg shell membrane which, in turn makes it more effective to adsorb dye in alkaline pH and increase the ionized able sites. The egg shell membrane composed of protein and polysaccharides which contained functional groups such as, hydroxyl, amine and sulfonic groups (depending on the pH of the aqueous solution) can react with the dye (Koumanova *et al*., 2002; Allen and Koumanova, 2005). Furthermore, the dye charges have been changed with pH values.

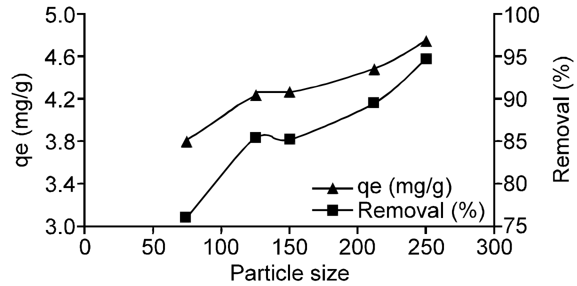

Fig. 6: The effect of ESM particle size on dye adsorption

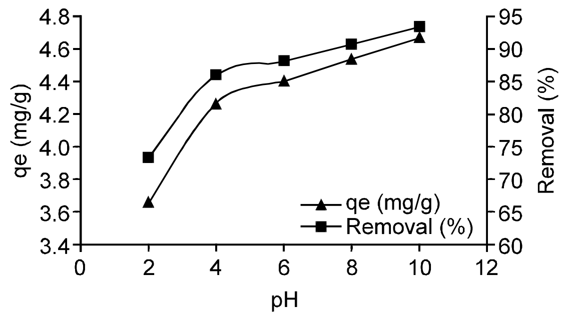

Fig. 7: The effect of pH on adsorption efficiency

The adsorption of methylene blue from aqueous solution by egg shell membrane at different temperatures was shown in Fig. 8. The results indicate that, increasing of temperature from 20-80°C lead to elevation of adsorbed dye from 3.3 mg/g to 3.86 mg/g. On the other hand, increasing the temperature to 100°C causes insignificant decreasing in dye adsorption (3.80 mg/g), at the same time, the removal percentage of dye was increased from 66% to 77.3% as the temperature rises from 20-80°C. These results showed that, the temperature is an another factor that can influence the efficacy of dye removal from solution. The phenomenon revealed that elevation of solution temperature increases the mobility of dye molecules and number of molecules that acquire sufficient energy to undergo an interaction with egg shell membrane surface (Hameed *et al*., 2007). Furthermore, increasing of temperature may leads to swelling effect within the internal surface of the egg shell membrane which enabling large quantities of methylene blue molecules to penetrate into the egg shell membrane structure (Ehrampoush *et al*., 2011).

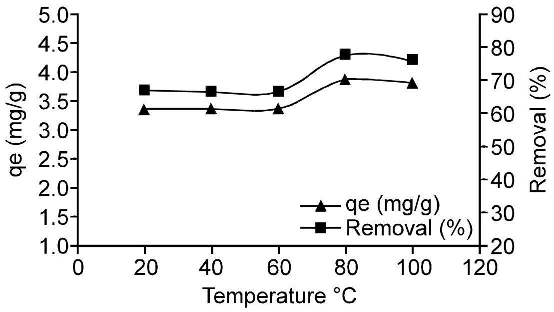

Fig. 8: The effect of temperature on adsorption efficiency

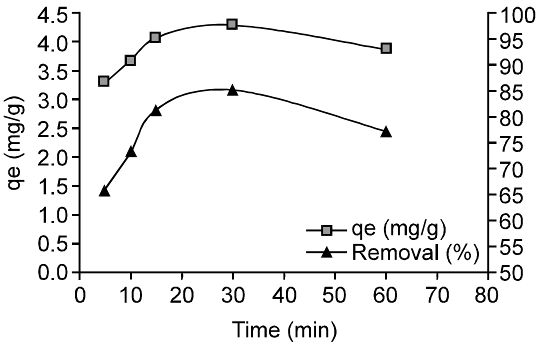

Fig. 9: The effect of contact time on adsorption efficiency

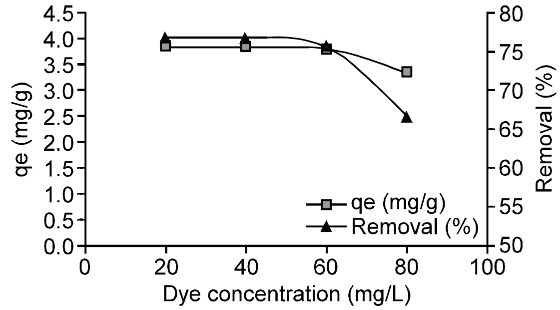

Fig. 10: The effect of dye concentration on adsorption efficiency

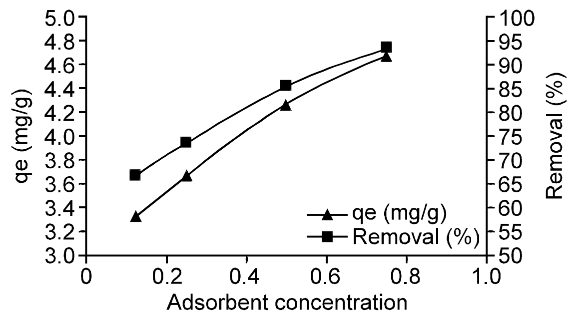

Fig. 11: The Effect of Adsorbent (ESM) concentration on dye efficiency

The effect of contact time on the dye adsorption was illustrated in Fig. 9. It was found that the egg shell membrane is very effective to remove dye from the solution. There was a proportional relationship between the contact time and the percentage of dye removal. As the contact time increase 5, 10, 15 and 30 min the percentages were 66%, 73.3%, 81.3% and 85.3% respectively, but there was a decline in the removal percentage showed after 60 min (77.3%). By increasing the contact 5, 10, 15 and 30 min, the dye adsorption were 3.30, 3.66, 4.06, 4.26 mg/g respectively.

Figure 10 showed the removal percentages at various dye concentrations at certain amount of adsorbent (1 g ESM). The results indicate that removal percentages decrease according to increase in dye concentrations it were 76.67%, 76.67%, 75.5%, 66.6% at concentrations 20, 40, 60, 80 mg/L respectively. Similarly, the adsorbed dye concentrations by ESM were 3.833, 3.833, 3.778 and 3.334 mg/g. The higher removal percentage of dye at lower dye concentration my refer to interact all methylene blue molecules in the aqueous solution with the binding sites of egg shell membrane but at higher concentrations the percentages of dye adsorption may affected by the overload concentration of the methylene blue, a situation that causing an adsorption disturbance on the adsorbent surface sites.

By increasing ESM concentrations in aqueous solution at certain dye concentration (10 mg/100 ml), the removal percentages of dye were increased (Fig. 11). It was 66.6, 73.3, 85.3 and 93.3% at concentrations 0.125, 0.25, 0.5 and 0.75 g ESM respectively. As a result, the adsorbed dye were 3.33, 3.66, 4.26 and 4.66 mg/g ESM respectively. These results indicate that, increasing adsorbent concentration provides sufficient surface area to interact with dye.

Conclusion: The egg shell membrane powder is an effective material that could be used as low cost adsorbent to remove anion and cationic dyes (like methylene blue) from water and wastewater at low concentration and short time. The dye concentration, the pH of dye solution, the temperature and the particle size of adsorbent were found as the more effective factors affecting the adsorption process. There is a need for new researches to develop the combination between egg shell membrane and other industrial dyes for more applications.

REFERENCES

Allen, S.J. and B. Koumanova, 2005. Decolourisation of water/wastewater using adsorption (Review). J. Univ. Chem. Technol. Metallurgy, 40: 175-192.

Asfour, H.M., O.A. Fadali, M.M. Nassar and M.S. El-Geundi, 1985. Equilibrium studies on adsorption of basic dyes on hardwood. J. Chem. Technol. Biotechnol., 35: 21-27.

Ehrampoush, M.H., Gh. Ghanizadeh and M.T. Ghaneian, 2011. Equilibrium and kinetics study of reactive red 123 dye removal from aqueous solution by adsorption eggshell. Iran. Environ. Health Sci. Eng., 8: 101-108.

Ghani, A.A., R. Santiagoo, A.C. Johnson, N. Ibrahim and S. Selamat, 2007. Dye removal from aqueous solution using egg shell powder, International conference on sustainable material, http://dspace.unimap.edu.my/dspace/bitstream/bitstream/123456789/1169/1/Dyi/20Removal%20from%20A.

Hameed, B.H., A.A. Ahmed and A.N. Aziz, 2007. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. Chem. Eng. J., 133: 195-203.

Juang, R.S., R.L. Tseng, F.C. Wu and S.J. Lin, 1996. Use of chitin and chitosan in lobster shell wastes for color removal from aqueous solution. J. Environ. Sci. Health, PartA, 31: 325-338.

Koumanova, B., P. Peeva, S.J. Allen, K.A. Gallagher and M.G. Healy, 2002. Biosorption from aqueous solution by egg shell membranes and *Rhizopus oryzae*: Equilibrium and kinetic studies. J. Chem. Technol. Biotechnol., 77: 539-545.

Mckay, G., J.F. Porter and G.R. Prasad, 1999. The removal of dye colours from aqueous solution by adsorption on low-cost materials. Water, Air, Soil Pollut., 114: 438-438.

Namasivayam, C. and N. Kanchana, 1993. Removal of Congo red from aqueous solution by waste banana pith. J. Sci. Technol., 1: 33-42.

Namasivayam, C. and D. Kavitha, 2002. Removal of congo red from water by adsorption on to activated carbon prepared from coir pith, an agriculture solid waste. Dyes Pigments, 54: 47-58.

Namasivayam, C., K.M. Dinesh, K. Selvi, B.R. Ashruffunissa, T.T. Vanathi and R.T. Yamuna, 2001. Waste coir pith-a potential biomass for the treatment of dyeing wastewaters. Biomass and Bioenergy, 21: 477-483.

Parsons, A.H., 1982. Structure of the eggshell. Poult. Sci., 61: 2013-2021.

Pramanpol, N. and N. Nitayapat, 2006. Adsorption of reactive dye by eggshell and its membrane. Kasetsat J.: Nat. Sci., 40: 192-197.

Rasheed, K.A., T. Hajira, F. Uddin and U. Hameed, 2005. Adsorption of methylene blue from aqueous solution on the surface of wool fiber and cotton fiber. J. Appl. Sci. Environ. Manage., 9: 29-35.

Sarioglu, M. and U.A. Atay, 2006. Removal of methylene blue by using biosolid. Global NEST J., 8: 113-120.

Tsai, W.T., J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin and C.W. Yeh, 2006. Characterization and adsorption properties of eggshells and eggshell membrane. Bioresour. Technol., 97: 488-493.

Tsai, W.T., K.J. Hsien, H.C. Hsu, C.M. Lin and C.H. Chiu, 2008. Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresour. Technol., 99: 1623-1629.

William, J.S. and J.C. Owen, 1995. Egg Science and Technology. 4th Edn., Food Product Press, New York, pp: 950.