METHYLENE BLUE REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON EGGSHELL BED

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Abstract:

Dyes and pigments have been used in many industries for colouration purpose. Dyes contain carcinogenic materials which can pose serious hazards to aquatic life and end users of the water. Therefore, it is important to remove these pollutants from wastewater before their final disposal. The initial concentrations of methylene blue (MB) dye were selected in the range of (20 and100) mg/L, the initial pH of dye solutions in the range (4 to 10) and adsorbent dose range (0.5 to 5)gm were investigated. The target adsorbent was prepared in laboratory conditions and pulverized by standard sieves at a range (0.3 to 0.85)mm particle size. The experimental adsorption isotherm was in good concordance with Langmuir and Freundlich models ($R^2 > 0.95$). increase of the eggshell dose led to decrease of the adsorbed dye per mass unit of the adsorbent.

Keywords: Eggshell**,** Methylene blue(MB), Isotherm model.

ازالة صبغة الميثيلين الزرقاء من المحاليل المائية بواسطة الامتزاز بطبقة من قشور البيض

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الخلاصة :

تستخدم الأصباغ في العديد من الصناعات منها الصناعات النسيجية ،المطاط، والورق وغيرها لتعطي لون معين لتلك المنتجات، فالمياه الخارجة من تلك الصناعات والتي تطرح إلى الأنهار تحوي تراكيز مختلفة من الأصباغ والتي تشكل مصدر مهم للتلوث فالكثير منها وخاصة العضوية تكون سامة وربما تؤثر على الحياة المائية.

تعتبر عملية إزالة الأصباغ من مياه الفضلات الخارجة من تلك الصناعات خطوة ضرورية لحماية البيئة إذ استخدمت تقنيات مختلفة لهذا الغرض. إما عن المواد المستخدمة للإزالة فهي إما مواد طبيعية مثل الفحم المنشط الذي يؤخذ من أنواع مختلفة من الأخشاب، أو تكون هذه المواد عبارة عن فضلات قد لا يستفاد منها ولكن في مجال ازالة الأصباغ يمكن الاستفادة منها بشكل كبير، مثل الفضلات الزراعية (قشور الرز ،قشور بذور زهرة الشمس) أو فضلات محلية مثل قشور البيض والتي استخدمت مطحونة كمادة مازة (مزيلة) لإزالة صبغة المثيلين الزرقاء من المحاليل المائية.

تم تغيير تراكيز الصبغة واختيرت بين (20-100) ملغم/ لتر، وقيمة الـ pH الأولية لمحاليل الصبغة تم تغييرها وتراوحت قيمتها بين (4-10)، كما تم تغيير كتلة المادة المازة وتراوحت قيمها بين (0.5-5) غرام في الفحوصات. المادة المازة المستخدمة تم تحضيرها في ظروف المختبر وتم تدريجها بمناخل قياسية بين (0.3- 0.85) مليمتر حجم حبيبي. مخطط الامتزاز التجريبي متفق بصورة جيدة مع معادلتي Langmuir و Freundlich وكانت قيمة معامل الترابط $R^2 > 0.95$.

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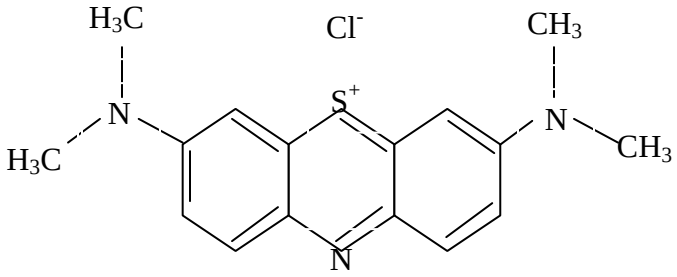
Introduction:

Dyes are chemical compounds have been used in many industries for coloration purposes such as, in food processing, textiles, papers, cosmetics and other industries. The effluents from these industries are the main sources of environmental dye pollution (Sarioglu and Atay, 2006). Over $7*10^5$ tonnes and approximately 10,000 different types of dye and pigment are produced world wide annually and the volume is steadily increasing (Iqbal and Ashiq, 2005).

Due to inefficiencies of the industrial dyeing process, some of the used dyes are lost in the effluents of textile units, rendering them highly colored (Malki et al., 2010). Direct discharge of these effluents causes formation of toxic materials in receiving media. In addition to their visual effects and their adverse impacts in terms of chemical oxygen carcinogenic (Dehghani et al., 2008).

Methylene blue (MB) was chosen for this study because of its known strong adsorption onto solids. MB is the most commonly used material for dying cotton, wood, and silk with molecular weight 373.9 corresponds to MB hydrochlorine with three groups of water. The structure of the MB is given as below (Azlinda et al., 2007)



In order to decrease the cost of treatment, attempts have been made to find low cost alternative adsorbents. Numerous approach have been made by various researchers to develop cheaper and effective adsorbents to remove dyes from a variety of starting materials from waste (Annadurai et al., 2002; Ozer et al., 2007). Eggshell used by enormous number of food manufactures and restaurants and the eggshell as a by- product represents approximately 11% of the whole egg weight is discard as waste. Many researchers have been done to make use of eggshell in different applications such as, fertilizers, feed additive and adsorption heavy metals and organic compounds from wastewater (Pramanpol and Nitayapat, 2006).

The chemical composition of eggshell (94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), as well as the porous nature of eggshell structure (7000-17000 pores). (William and Owen, 1995) makes it an attractive material to serve as an adsorbent agent. Furthermore, the inner eggshell membrane has good adsorption characteristics due to its composition (polysaccharides fibers and collagen like protein), which containing substituting group sites such as hydroxyl, amine and sulfonic groups can react with dye (Allen and koumanova, 2005).

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(Nuttawan and Nuttakan, 2006) Examined the possibility of using eggshell and its membrane as adsorbents for the removal of reactive dyes from industrial wastewater.
(Ehrampoush et al., 2011) Evaluated the feasibility of eggshell for reactive red 123 dye removal from aqueous solution and determination of adsorption equilibrium and kinetics.
(Dhuha et al., 2012) studied the utilization of eggshell and its membrane as a dye discard material for three different types of dyes to remove them from their aqueous solutions and determine the optimum conditions for the dye adsorption.
(Carvalho et al., 2011) Investigated the adsorption process both on simulated and real effluents onto eggshell-derived adsorbent. This was accomplished by analyzing the uptake potential for selected contaminants. Real wastewater effluents were studied to determine the effectiveness of this low cost adsorbent. Results obtained shown that eggshell can remove several pollutants from different types of aqueous systems, with great efficiency.

This study investigate the potential of eggshell as a low cost adsorbent for MB removal. The adsorption was carried out to study different initial MB concentrations, different values of pH and different quantities of dose of adsorbent using batch technique. Data were analyzed using Langmuir and Freundlich isotherm models.

Materials and methods:

1- Adsorbate :

Basic dye used in this study was methylene blue purchased from scientific bureaus in Iraqi commercially markets. MB has molecular formula (C_{16} H_{18} N_3CIS) , (Mol. wt 373.91 g/mol). (Hadeel, 2011). The wave length of this dye is 664.5 nm. The dye stock solution was prepared by dissolving accurately weight dye in distilled water to the concentration of 1 g/L. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations.

2-Preparation of eggshell:

Eggshells were collected from local restaurants, washed with tap water and dried in the oven. The dried eggshell with membrane were grounded separately by house mill to prepare granular eggshell with different particle sizes (0.3-0.85)mm by using a standard sieves set. The sieved materials were tested for their adsorbent qualities without further chemical or physical treatment.
The relevant surface properties and predominant constituents of eggshell are presented in table 1.

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Table 1: constituents and surface relevant characteristics of eggshell

Component	value
Ca	61.5%
Mg	1.94%
P	28.34%
S	8.2%
Surface area	1.2 m^2/g
Total pore volume	0.0062 cm^3/g

3-Determination of MB:

The concentrations of MB in aqueous solutions were determined by measuring the absorbance of the solution at 664.5 nm using a uv-visible spectrophotometer type (uv 1600 pc shimadzu). Aqueous solutions of the dye within the concentration range (0-30)mg/l were used for calibration. Plots of absorbance against concentration were linear as shown in figure 1.

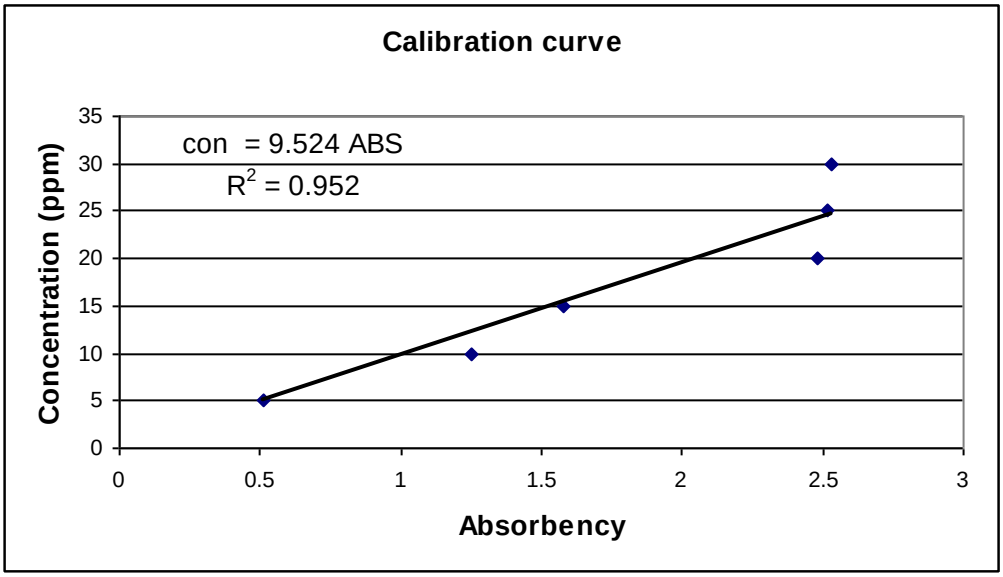

Fig 1:Calibration curve

4- Batch experiment :

Batch adsorption experiments were carried out aliquots of 250 ml of MB solution of (100 ppm) poured into conical flasks containing accurately weighed a mounts of the eggshell range from (0.5- 5)gm. Conical flasks were shaken during the batch experiments by a shaker set to 150 rpm, at constant temperature of 25 C°. After shaking the flasks for equilibrium time, the mixtures were filtered through filters papers to remove any suspended adsorbent. Final concentrations of MB were determined by using UV- visible spectrophotometer in higher studies laboratory in agricultural college,

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Babylon university. All the experiments were carried out personally in sanitary laboratory of environmental department of engineering college at July, 2012.

Adsorption experiments :

All the adsorption experiments were carried out by batch technique. The initial concentrations of MB dye in the experiments were selected in the range of (20-100) ppm. The dye solution (50 ml) of desired concentration at neutral pH was taken in Al-covered glass vials and agitated with a known weight of egg shell at room temperature in a shaker set at 150 rpm for a desired time periods.

A contact time of 2 h (Ehrampoush et al., 2011) was selected for the entire equilibrium test. the solution pH was carefully adjusted by adding a small amount of Hcl and Naoh solutions (0.1 N), which measured using a pH meter.

The amounts of adsorbed dye at equilibrium and dye removal efficiency were calculated from the mass balance equation 1 and equation 2, respectively, as follows:

$$q_e = \frac{V}{M} * (C_o - C_e) \qquad \ldots\ldots\ldots 1$$

$$E = \frac{C_o - C_e}{C_o} * 100 \qquad \ldots\ldots\ldots\ldots 2$$

Where:

C_e and C_o are the equilibrium and initial concentrations of dye (mg/l), respectively; q_e is the equilibrium dye concentration on adsorbent (mg/g); V is the volume of dye solution (L); M is the mass of adsorbent (g) and E is the removal efficiency (Karaoglu et al., 2009; Ghanizadeh et al., 2010). The effect of adsorbent dosage was studied by changing the amount of egg shell from (0.5-5) gm.

Isotherm equations:

The Freundlich and Langmuir models were used to describe the equilibrium between the adsorbate and the adsorbent which can be represented respectively as follows (Farah et al., 2007)

$$Log q_e = \log k + \frac{1}{n} \log C_e \qquad \ldots\ldots\ldots\ldots 3$$

K and n are constants that depict the adsorption capacity and intensity, respectively.
The linear form of the Langmuir isotherm equation can be described as :

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \qquad \ldots\ldots\ldots\ldots 4$$

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q_m is the maximum amount of adsorption (mg/g) and b is the adsorption equilibrium constant (L/mg). The experimental data were analyzed according to linear form of isotherm equations 3,4.

In order to describe the adsorption process type and the adsorption affinities between the adsorbent and the adsorbate, the dimensionless separation factor R_L was calculated from the following formula $R_L = \frac{1}{1+bC_o}$. (Hameed et al., 2007; Bayramoglu et al., 2009; Ghanizdeh et al., 2010). For which

Type of adsorption	Favorable	Linear	Irreversible	Unfavorable
R_L Value	< 1	1	0	> 1

Other isotherms equations are:

Temkin isotherm :

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy .

The Temkin isotherm is given as:

$qe = BlnA + B \ln Ce$ (9) …… 5

where A (l/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption. A

plot of *qe* versus ln *Ce* enables the determination of the isotherm constants B and A from the slope and intercept of the straight line plot. **(**Oladoja et al., 2008).

Sips isotherm:

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and expected to describe heterogeneous surfaces much better. At low adsorbate concentrations it reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. (Zohre et al., 2010) . The model can

be written as:

$$q_e = \frac{q_m a_s c_e^{\frac{1}{n}}}{1 + C_e^{\frac{1}{n}}} \quad \text{…… 6}$$

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Where; *m q* is monolayer adsorption capacity (mg g-1) and *s a* is Sips constant related to energy of adsorption and parameter *n* could be regarded as the parameter characterizing the system heterogeneity.

Effect of pH on adsorption:

The pH of methylene blue solutions were adjusted to (4, 6, 8, 10) pH values at dye concentration (100 mg/L). the dye concentration was determined by measuring the absorbance of the solution at 664.5 nm.

Effect of dosage of eggshell on adsorption :

Different amounts of eggshell (0.5, 1, 2, 3, 4 and 5) gm were mixed with methylene blue solution at concentration (100 mg/L) and (pH 6).

Effect of dye concentration on adsorption :

Fives grams of eggshell were mixed with 50 ml of methylene blue solution of different concentration (20, 25, 40, 50,70 and 100)mg/L.

Results and discussions:

1- Equilibrium isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being adsorbed. At this point the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm.

The most widely used isotherm equation for design of adsorption systems are Langmuir and Freundlich equations. MB concentration was kept constant (100 mg/L) at (0.5, 1, 2, 3, 4and 5)gm of eggshell.

Application of Langmuir and freundlich models to the adsorption isotherm showed that this models provided excellent satisfactory with the highest R^2 (0.97 and 0.95). The estimated values for the parameters of the these models are demonstrated in table 2. Based on dimensionless separation factor (R_L) on Langmuir model the value of this parameter for MB within eggshell is lower than 1 which confirms that adsorption of this dye with this material is a good treatment under the conditions of this research.

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Table 2: Isotherm constants for MB removal by eggshell

Freudlich		Langmuir	
K(mg/g)(L/mg)	$3.47*10^{-7}$	b (L/mg)	0.04
1/n	5.29	q_m (mg/g)	0.5
R^2	0.952	R^2	0.974

The Langmuir and Freundlich isotherms are compared to each other for eggshell experiment and are given in figure 2.

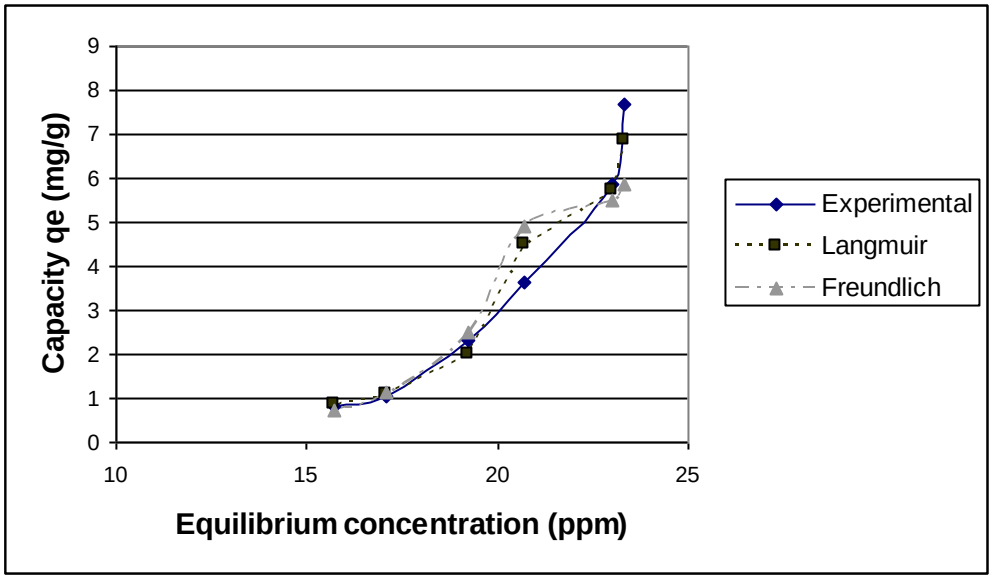

Fig. 2: Isotherm of MB on eggshell

The dominant elements in eggshell structure were calcium and phosphorous as $CaCO_3$ and $Ca_3(PO_4)_2$, this represent that the eggshell can be categorized as a homogeneous adsorbent which contains a round 95% Ca and has only 4% organic mater. The specific surface area of eggshell was 1.2 m^2/g, the sizes of the pores were lower than (20 nm) and did not have uniform sizes. (Ehrampoush et al., 2011).

2- Effect of pH :

The pH of aqueous solutions is a key factor on adsorption process which is function of hydrogen and hydroxyl ions concentrations.

The effects of solution pH on MB adsorption within eggshell were investigated and the results are illustrated in figure 3, which shows that the elevation of pH leads to increasing of the adsorbed mass of pollutant (q_e) onto eggshell.

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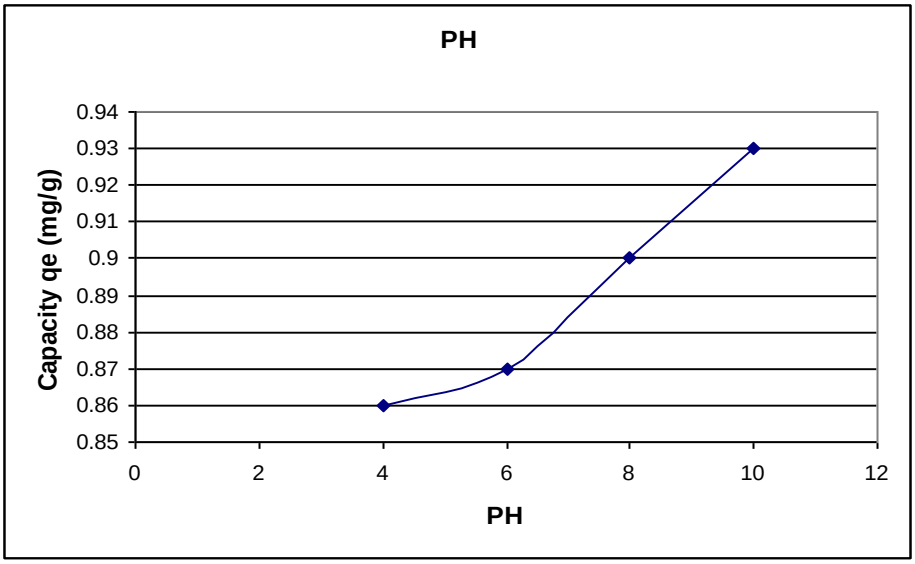

Fig. 3: Effect of pH on adsorption efficiency

When the pH of aqueous solution increased from (4 to 10), q_2 increased from (0.86 to 0.93)mg/g, similarly, a higher removal percentages of MB from solution were observed (86%, 87%, 89.3%, 93.4%) at pH (4, 6, 8, 10) respectively. These results can be attributed to the effect of the solution pH on the charge of reactive group within eggshell membrane which, in turn makes it more effective to adsorb dye in alkaline pH and increase the ionized able sites.

The eggshell 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.

3-Effect of adsorbent dose

Variation of adsorbent dose showed that although increasing of eggshell dose in aqueous solution can result to increased pollutant removal, but this elevation of eggshell leads to decreasing of adsorbed dye per unit of adsorbent (q_e); this phenomenon may be related to the use of surface area as unsaturated form.

The results of this research showed that with increasing of eggshell from (0.5 – 5)gm, the q_e (mg/g) decreasing from (7.67 – 0.84) mg/g, Figure 4.

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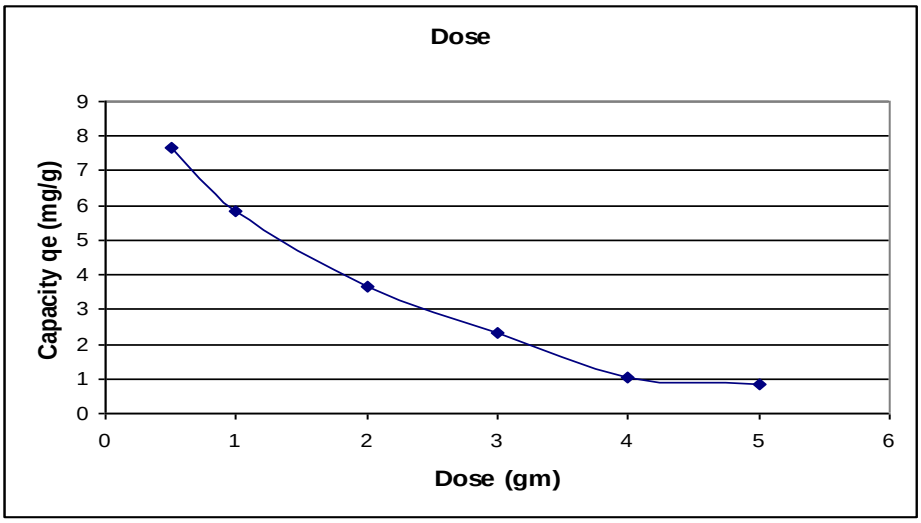

Fig. 4: Effect of adsorbent dose on adsorption efficiency

Although increasing of the eggshell dose led to increasing of dye removal efficiency (76%, 757%, 77.5%, 80.2%, 82.9%, 84.3%) but resulted in decreasing of adsorbed dye per mass unit of eggshell (7.67 to 0.84) mg/g. This result may be related to occupation patterns of active sites and may be in higher doses of eggshell, the active sites of adsorbent occupied as unsaturated form that may be related to particles aggregation and overlapping interfere with binding sites which reduces the total surface area and adsorption quantity. (Yeddou and Bensmaili, 2007; Mezenner and Bonsmaili, 2009).

4 -Effect of dye concentration

Increasing of MB dye concentration led to increasing of q_e (mg/g), (0.16 to 0.84)mg/g . this phenomenon may be related to the driving forces that need to overcome for the resistances of pollutants migration from the aqueous solutions to the eggshell surface (Hameed and Ahmad, 2009), this results shown in figure 5.

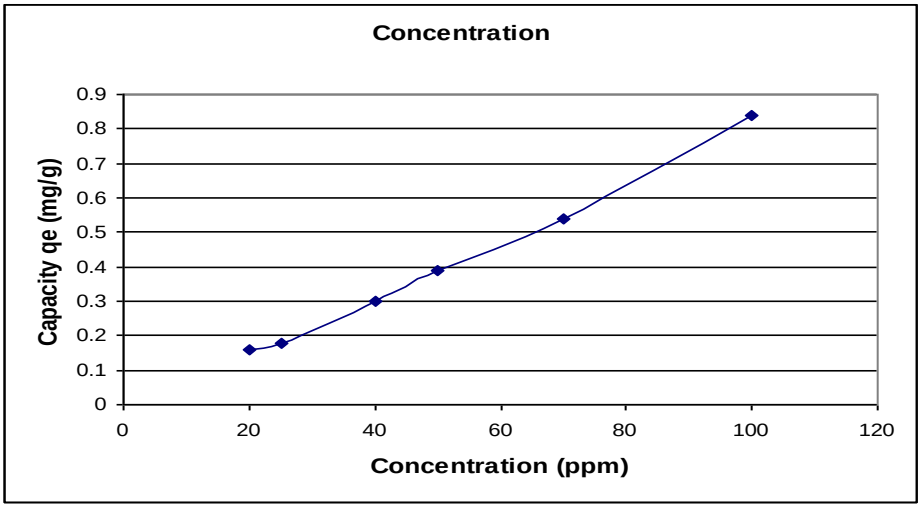

Fig. 5: Effect of dye conc. on adsorption efficiency

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The percentage of removal at various concentration (20, 25, 40, 50, 70 and 100) ppm using same amount of adsorbent was studied and demonstrated in table 3.

Table 3:Percentage removal of MB on eggshell

Con.	20	25	40	50	70	100
% R	84	83	79	77	75	73

The removal percentage showed a decreasing trend as the initial MB concentration was increased. At lower concentrations all MB present in the adsorption medium could interact with the binding sites so higher adsorption removal were obtained. At the higher concentrations lower adsorptions removed were observed because of the saturation of the adsorption site. (Azlined et al., 2007).

Conclusion :

- The eggshell waste which easily and abundantly available was using as a good adsorbent for methylene blue removal.
- Using eggshell as an adsorbent give an effective and useful disposal of this material.
- The adsorption obeyed both Langmuir and Freundlich isotherm models.
- The ability of eggshell to adsorb methylen e blue was investigation as a function of adsorbent dosage, pH, and initial dye concentration. The removal of methylene blue increases with increase of adsorbent dosage used and initial dye concentration.
- The eggshell is cheap and available material in large quantities, so no regeneration is necessary.
- On the bases of this study, eggshell may also be effective in removing other harmful species, such as heavy metal ions.

References:

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

Annadurai, G., Juang, R.S., and Lee D.J., (2002)."Use of cellulose-based waste for adsorption of dyes from aqueous solutions". Journal of Hazardous Materials B92: 263-274

Azlinda Abdul Ghani, Ragunathan Santiagoo, Anbu Clemensis Johnson, Naimah Ibrahim, Salsuwanda Selamat, (2007). "Dye removal from aqueous solution using eggshell powder". School of Environmental Engineering. Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia.

Bayramoglu, G., Altintas, B., Arica, M.Y., (2009). "Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin", Chem. Eng. J, 152 (2-3): 339- 346.

ISSN 2072-3875

Carvalho J., Ribeiro A., Graça J., Araújo J., Vilarinho C. and Castro F., (2011). " Adsorption process onto an innovative eggshell-derived low-cost adsorbent in simulated effluent and real industrial effluents", wastes: Solutions, Treatments and Opportunities 1St International Conference September 12th – 14th.

Dehghani, M.H., Mesdaghinia, A.R., Nasseri, S., Mahvi, A.H., Azam, K., (2008). "Application of SCR technology for degradation of reactive yellow dye in aqueous solution". Water Qual. Res. J. Can. 43 (2/3): 1-10.

Dhuha D. Salman, Wisam S. Ulaiwi and N.M. Tariq, (2012). "Determination the Optimal Conditions of Methylene Blue Adsorption by the Chicken Egg Shell Membrane". Iraq. International Journal of Poultry Science 11 (6): 391-396.

Ehrampoush, M. H., Ghanizadeh, Gh., Ghaneian, M. T., (2011). "Equilibrium. Health. Sci. Eng., Vol. 8, No. 2, pp. 101-108, Iran. and kinetics study of reactive red 123 dye removal from aqueous solution by adsorption on eggshell". J. Environ

Farah, J.Y., EL-Gendy, N.S., Farahat, L.A., (2007). "Biosorption of Astrazone Blue Basic dye from an aqueous solution using dried biomass of Baker's yeast". J. Hazard Mater, 148 (1-2): 402-408.

Ghanizadeh, Gh., Ehrampoush , M.H., Ghaneian, M.T., (2010). "Aplication of Iron Impregnated Activated Carbon for Removal of Arsenic from Water". Iran. J. Environ. Health. Sci. Eng. 7 (2): 145-156.

Hameed B.H., Din A.T.M., and Ahmad A.L., (2007). "Adsorption of methylene blue onto bamboo- based activated carbon : Kinetics and equilibrium studies". Journal of Hazardous Materials 141: 819-825.

Iqbal, M.J.and Ashiq, M.N., (2005). "Adsorption of dyes from aqueous solutions on activated charcoal". Journal of Hazardous Materials B139: 57-66.

Karaoğlu, M.H., Doğan, M., Alkan, M., (2009). "Removal of cationic dye by kaolinite, Microporous Mesoporous Mater". 122 (1-3): 20-27.

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.

Maleki, A., Mahvi, A.H., Ebrahimi, R., Zandsalimi, Y., (2010). "Study of photochemical and sonochemical processes efficiency for degradation of dyes in aqueous solution", Korean J. Chem. Eng., 2DOI: 10.1007/s11814- 010-0261-0

Mezenner, N.Y., and Bensmaili, A., (2009). "Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste". Chem Eng J. 147 (2-3) : 87-96.

Nuttawan Pramanpol and Nuttakan Nitayapat, (2006). " Adsorption of Reactive Dye by Eggshell and Its Membrane". Kasetsart J. (Nat. Sci.) 40 (Suppl.) : 192 – 197.

OLADOJA N. A., ABOLUWOYE C. O. , OLADIMEJI Y. B., (2008). " Kinetics and Isotherm Studies on Methylene Blue Adsorption onto Ground Palm Kernel Coat". Turkish J. Eng. Env. Sci. 32: 303 – 312.

ISSN 2072-3875

Ozer D., Dursun G.and Ozer A., (2007). "Methylene blue adsorption from aqueous solution by dehydrated peanut hull". Journal of Hazardous Materials 144:171-179.

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

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

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

Yeddou, N., and Bensmaili, A., (2007). "Equilibrium and kinetic modeling of iron adsorption by eggshell in a batch system: effect of temperature. Desalination". 206: 127-134.

Zohre Shahryari, Ataallah Soltani Goharrizi* and Mehdi Azadi, (2010). " Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes". International Journal of Water Resources and Environmental Engineering Vol.2 (2), pp. 016-028.

ISSN 2072-3875