EQUILIBRIUM AND KINETICS STUDY OF REACTIVE RED 123 DYE REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON EGGSHELL

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ABSTRACT

The aim of this study was to determine the equilibrium and kinetics adsorption of reactive red 123 dye (RR 123) from aqueous solution with chicken's eggshell as an adsorbent. The initial concentrations of reactive red 123 dye were selected in the range of 25 and 50 mg/L. The target adsorbent was prepared in laboratory conditions and pulverized by ASTM standard sieves. Measurement of the adsorbent surface area was carried out via Brunauer-Emmett-Teller isotherm. The experimental data were analyzed with Langmuir, Freundlich and Temkin isotherm models. The results showed that the calcium components were the main constituents of eggshell (around 95% Ca). The experimental adsorption isotherm was in good concordance with Langmuir and Freundlich models ($R^2 > 0.90$) and based on the Langmuir isotherm the maximum amount of adsorption (q_{max}) was 1.26 mg/g. Increase of the eggshell dose and the solution temperature beyond 45ºC led to decrease of the adsorbed dye per mass unit of the adsorbent, but increase of the solution pH up to 9 led to the improvement of dye adsorption. The kinetic studies revealed that the adsorption of reactive red 123 was rapid and complied with pseudo-second order kinetic ($R^2 = 0.99$), with the kinetic constant of 0.02 g/mg.min.

Key words: Eggshell waste; Reactive red 123 dye; Adsorption; Sorption kinetics; Natural sorbent

INTRODUCTION

Synthetic dyes are extensively used in the textile industry. 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 (Boer *et al*., 2004; Maleki *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 demand, many synthetic dyes are toxic, mutagenic and carcinogenic (Rezaee *et al*., 2008; Dehghani *et al*., 2008).

Degradation of dyes, especially the reactive dyes is difficult, due to their complex structure, water solubility and synthetic nature. Therefore, it is necessary to find the effective methods of wastewater treatment capable of removing color and toxic organic compounds from textile effluents (Netpradita *et al*., 2004; Mahvi *et al*., 2009).

Current studies show that adsorption is one of the most promising techniques for quick lowering of the concentration of dissolved dyes from aqueous solutions (Aksu, 2005). In this regard, activated carbon has been evaluated extensively for the removal of color resulting

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from the different classes of dyes and is now the most widely used adsorbent for dyes.

The application of carbon-based adsorbent still remains an expensive process due to the high cost in the using of activated carbon and difficulties in regeneration of the spent activated carbon. Hence, there is growing interest in utilizing biomass wastes/alternatives to activated carbon as low-cost adsorbents (Tsai *et al*., 2008 a).

Based on the bioresource recovery and reuse, the high value of the utilization of eggshell (ES) waste known as a food processing by-product, has slightly increased in recent years. The use of chicken eggshell has been introduced as a possible bone substitute, as the starting material for preparing calcium phosphate bioceramics (e.g., hydroxyapatite), and as a low-cost adsorbent for removal of ionic pollutants from aqueous solutions (Tsai *et al*., 2008 b). The objective of this research was to evaluate the feasibility of eggshell for reactive red 123 dye removal from aqueous solution and determination of adsorption equilibrium and kinetics.

MATERIALS AND METHODS

Reagents and analytical procedure

Reactive red 123 dye (RR123) was obtained commercially from Dye Star Company and used as an adsorbate without purification. It was dried at 110°C for 2 h before use (Sariglu and Aatay, 2006). Dye aqueous solutions were prepared with tap water. All other chemicals were guaranteed or analytic grade reagents commercially available and used without further purification. Because the maximum absorbance wavelength (λ_{max}) of RR 123 was not reported in other studies, this parameter was determined with absorbance spectrum detection between 200 nm to 800 nm using the UV-visible spectrophotometer (PU 8700). The absorbance spectrum curve showed that the λ_{max} of RR 123 was 506 nm. The concentration of dye was measured at this λ_{max} with the calibration curve which was prepared by the use of the standard solutions of RR 123.

Preparation of eggshell

Granular eggshell was prepared in the laboratory conditions (20-25 °C). The eggshell obtained from commercial confectionaries were crushed into pieces of 10-15 mm in length , rinsed three times with distillated water and pulverized by standard ASTM sieves with the range of 8.00 to 14.00 mesh (2.83-1.41 mm) (Purevsuren *et al*., 2004; Choy and McKay., 2005 ; ASTM, 2007 **)**. The effective size (D_{10}), D_{60} and uniformity coefficient (UC) of the adsorbent were 3.00 mm, 5.10 mm and 1.70, respectively. The prepared eggshell was dried at 100-110 °C over night, cooled in a desiccator and used as an adsorbent in the experiments (Rezaee *et al*., 2009).

Characterization of eggshell

The chemical composition and solid structure of ES was analyzed using scanning electronic microscopy and energy dispersive analysis X-ray (EDAX) spectra (Model XL30 Philips). Other surface specifics of ES were characterized by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) isotherms (Orfão *et al*., 2006; Ghanizadeh *et al*., 2010). The BET and BJH specific surface areas were determined by nitrogen adsorption-desorption measurement and applying of the relevant equations within P/P_0 0-1 (P and P_0 represent the operational and absolute pressures, respectively) (Vágvölgyi *et al*., 2008). Also, the porosity of ES was determined with the conventional adsorption of N_2 gas at 77 °K and pressure of 91.43 KP (Shieldes *et al*., 2004). Analysis of data for calculation of the BET and BJH surface areas (m^2/g), pore volume and porosity was carried out by Belsorb software (Ver.5) (data not shown).

Adsorption experiments

All the adsorption experiments were carried out by batch technique. The kinetic adsorption studies were performed at different doses of adsorbent, pH and dye concentrations. The initial concentrations of RR 123 dye in the experiments were selected in the range of 25 to 50 mg/L. 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 ES at room temperature (25±0.5 °C) in a shaker set at 150 rpm (GFL 3017) for a desired time periods.

The preliminary kinetic experiments revealed that 120 min was long enough to achieve the equilibrium. Therefore, a contact time of 2 h

was selected for the entire equilibrium test. The solution pH was carefully adjusted by adding a small amount of HCl and NaOH solutions (0.1N), which measured using a pH meter (Mettler 8603). At the end of adsorption tests, the suspensions were centrifuged for 5 min at 2000×g and the concentrations of residual dye were determined using Philips UV/ visible PU 8700 spectrophotometer corresponding to λ_{max} of RR 123 (506 nm). Blank solution with no dye was used for each series of experiments. Dilutions were carried out when measurement exceeded the linearity of the calibration curve. 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:

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

$$E = \frac{C_o - C}{C_o} \times 100 \qquad (2)$$

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 (Karaoğlu *et al.*, 2009 ; Ghanizadeh *et al.*, 2010). The effect of adsorbent dosage was studied by changing the amount of ES mass from 1 to 5 g.

Adsorption characteristics
In adsorption systems the accurate determination of the maximum adsorption capacity used for process design is important. The Freundlich, Langmuir and Temkin models were used to describe the equilibrium between the adsorbate and the adsorbent, which can be represented respectively as follows (Farah *et al.*, 2007):

$$\log qe = \log k + \frac{1}{n} \log C_e \qquad (3)$$

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:

$$\frac{1}{q_e} = \frac{1}{q_{max} \times b C_e} + \frac{1}{q_{max}} \qquad (4)$$

q_{max} is the maximum amount of adsorption(mg/g) and b is the adsorption equilibrium constant(L/mg).
Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln (K_t C_e) \qquad (5)$$

The linear form of this equation can be expressed as:

$$q_e = B \ln K_t + B \ln C_e \qquad (6)$$

where: $B = \dfrac{RT}{b}$ in which T is the absolute temperature in $^\circ$K and R is the universal gas constant in (j/mol$^\circ$K), respectively. In this model K_t is the binding constant which represents the maximum binding energy and constant B is related to the heat of adsorption (Hameed *et al.*, 2007).
The experimental data were analyzed according to linear form of isotherm equations (Eq$_s$ 3, 4, and 6). Analysis of data for selection of the best fit isotherm as carried out by linear regression analyses of these models and comparison of the correlation coefficients (R^2) (Farah *et al.*, 2007). In order to describe the adsorption process type and the adsorption affinities between the adsorbent and adsorbate, the dimensionless separation factor R_L was calculated from the following formula $R = \dfrac{1}{1 + b\,C_o}$ (Hameed *et al.*, 2007; Bayramoglu *et al.*, 2009; Ghanizadeh *et al.*, 2010) for which:

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

Kinetic parameters and energy of adsorption

The kinetic of RR123 dye adsorption on ES was evaluated with the pseudo-first order and pseudo-secondorder models. For the analysis of data with the first model, the linear form of Lagergren equation was used, which its integrated form can be expressed as:

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.203} \, t \qquad (7)$$

where q_t is the amount of dye adsorbed per unit weight of adsorbent at time t (mg/g) and k_1 is the rate constant for pseudo-first order kinetic which can be calculated from the plot of $\log (q_e \cdot q_t)$ versus time. Since this model may not fully describe the adsorption kinetics, we used the pseudo-second-order equation. This model is often successfully used to describe the kinetics of fixation reaction of adsorbate on adsorbent surface. The linear and integrated form of this model can be described as:

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^{\,2}} + \frac{1}{q_e} \, t \qquad (8)$$

where k_2 is the rate constant of adsorption. The equilibrium adsorption capacity (q_e) and the rate constant k_2 (g/mg.min) were determined with plot of (t/ q_e) versus time (Yu *et al*., 2009).

RESULTS

Adsorbent characteristics

The results of energy dispersive X-ray (EDX) spectra analysis demonstrate that calcium is the main component of ES (Fig. 1). As shown in Table 1, analysis of ES component with EDX showed that calcium and phosphorous as $CaCO_3$ and $Ca_3(PO_4)_2$, respectively, were the dominant elements in ES structure. These results represent that the ES can be categorized as a homogeneous adsorbent which contains around 95% Ca and has only 4% organic mater. Analysis of surface characteristics with BET and BJH models showed that the specific surface area of ES was 1.2 m^2/g and the sizes of the pores were lower than 20 nm. Also, BJH analysis showed that the pores of this adsorbent did not have uniform sizes (data not shown).

Effect of adsorbent dose

Variation of adsorbent dose showed that although increasing of ES dose in aqueous solution can result to increased pollutant removal, but this elevation of ES 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 ES from 0.5 g to 5 g, the q_e (mg/g) decreased from 0.82 mg/g to 0.4 mg/g (Fig. 2). This result indicates that
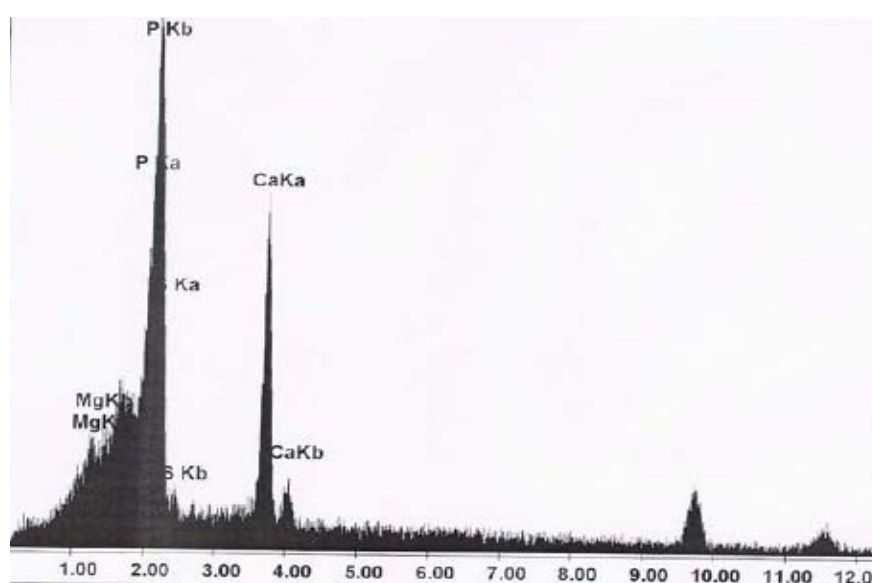

Fig.1: EDX analysis of Egg Shell with 15000 x

Table 1: Constituents and surface relevant characteristics of ES

Component	Value
Ca	61.5%
Mg	1.94%
P	28.34%
S	8.2%
BET surface area	1.20 m^2/g
BJH surface area	1.10 m^2/g
Total pore volume	0.0062 Cm^3/g

although mass elevation of adsorbent can provide large or available surface area, but the adsorption pattern of the pollutant as unsaturated form leads to unfavorable using of adsorbent. This phenomenon is the most important point for the design of economical and large scale adsorption devices.
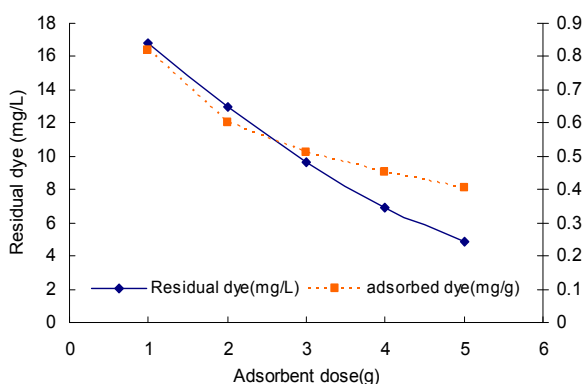

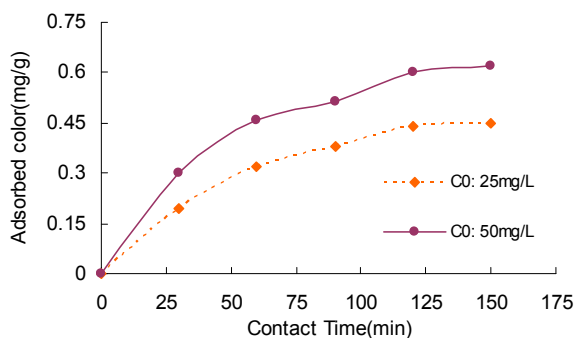Fig. 2 : Effects of adsorbent dosage on RR 123 adsorption efficiency

Fig. 3 : Effects of dye concentration and contact time on adsorption efficiency

Effects of dye concentration and contact time

The effects of contact time and initial concentration of dye on RR123 adsorption at room temperature are shown in Fig 3. The quantity of adsorbed solute (mg/g) increased with lapse of contact time and the equilibrium reached after 120 min. This figure shows the adsorption or migration rate of dye molecules from liquid to solid phase. The q_e for C_0= 25 and 50 mg/L were 0.45 mg/g and 0.62 mg/g, respectively. These results implies that the removal of RR 123 with ES depends on dye concentration and may be related to driving forces that need to overcome for the resistances of pollutants migration from the aqueous solutions to the ES surface.

Effects of pH and temperature

The relevant surface properties and predominant constituents of ES are presented in Table 1. The pH of aqueous solutions is a key factor on adsorption process which is a function of hydrogen and hydroxyl ions concentrations. The effects of solution pH on RR 123 adsorption within ES were investigated and the results are illustrated in Fig. 4, which shows that the elevation of pH leads to increasing of the adsorbed mass of pollutant (q_e) onto ES. When the pH of aqueous solution increased from 5 to 9, q_e increased from 0.3 to 0.5 mg/g. Based on this phenomena it can be concluded that elevation of the aqueous pH to higher scale may lead to increasing of ionisable charge sites and adsorbed dye on the ES surface. Temperature of the adsorption process is another factor that can influence the efficacy of these systems. In this research the effect of temperature on RR 123 adsorption within ES was studied (Fig. 5). This figure shows that the fluctuation of temperature in studied range has different effects on RR 123 adsorption with ES. As shown in Fig. 5, increasing of temperature from 15 to 25° C leads to elevation of adsorbed dye from 2.61 mg/g to 2.78 mg/g , but temperature increase from 25ºC to 55ºC causes the decreasing of q_e to 1.49 mg/g. These results show that, although the enhancing effects of temperature on RR 123 adsorption is not important, but inhibition effects of the higher temperatures are significant and should be considered as an operational parameter in economical equipments.
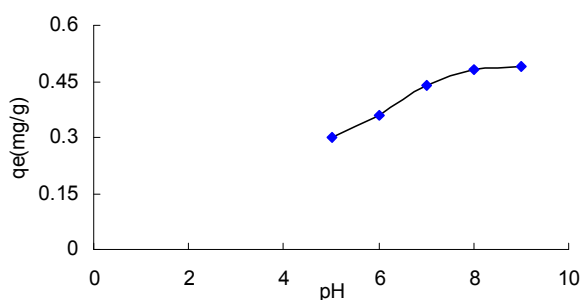
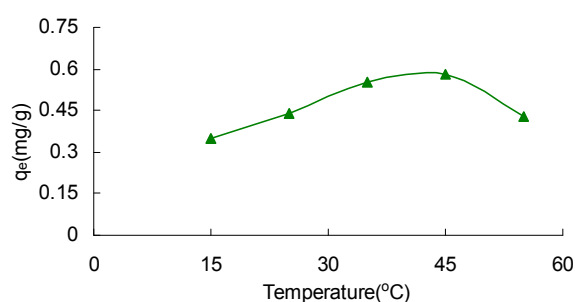Fig. 4: Effect of pH on dye adsorption on the eggshell

Fig. 5 : Effect of temperature on dye adsorption on the eggshell

Sorption experiments/Adsorption isotherm
Application of Langmuir, Freundlich and Temkin models to the adsorption isotherm, showed that the Freundlich and Langmuir isotherm models provided excellent satisfactory with the highest R^2 value (0.93 and 0.91) compared to the Temkin model. The estimated values for the parameters of these models are demonstrated in Table 2.

Although the correlation coefficient of the Freundlich isotherm is slightly higher than the Langmuir isotherm, but the experimental studies with other operational parameters such as pH and temperature showed that the calculated q_e (mg/g) in various pH and temperature complies with q_e that was determined with Langmuir isotherm; so, it can be derived that the Langmuir isotherm gave better fits than the other isotherms in which the maximum uptake capacity for RR 123 was 1.26 mg/g. Based on dimensionless separation factor (R_L) on Langmuir model the value of this parameter for RR 123 adsorption within ES is lower than 1 which confirms that adsorption of this dye with this material is favorable under the conditions of this research.

The results of the kinetics of adsorption process are shown Table 3, Analysis of data and regression coefficient (R^2) represent that the adsorption of this dye complies with pseudo- second order kinetic. Thus the correlation coefficient of this model is higher than 0.99 and the calculated adsorption capacity complies with experimental values. The values of k_1 and k_2 were calculated as 0.041 and 0.063 g/mg.min for pseudo- first order and pseudo-second order kinetics, respectively.

DISCUSSION
As shown in Table 1 and Fig. 1, the dominant constituents of ES are Ca and P. Similar results were reported by Tsai *et al* (2006). Table 1 shows the BET surface area and the pore volume of ES were determined to be 1.2 m²/g and 0.0062

Table 2: Characteristics of adsorption isotherms

Freundlich		Langmuir		Temkin	
$k(mg/g).(L/mg)^{1/n}$	27.5	b(L/mg)	0.082	$k_t(L/mg)$	0.67
n	0.57	$q_{max}(mg/g)$	1.26	B	0.304
R^2	0.93	R^2	0.91	R^2	0.86
		R_L	0.33		

Table 3: Kinetics constants of RR 123 adsorption onto eggshell

Kinetic model	k_2 , (k_1)		q_e(mg/g)		R^2	
	C_0: 25mg/L	C_0:50 mg/L	C_0:25mg/L	C_0:50 mg/L	C_0:25mg/L	C_0: 50 mg/L
Pseudo-second order (g/mg.min)	0.0195	0.019	0.7	0.9	0.99	0.99
Pseudo-first order (1/min)	(0.099)	(0.025)	0.6	0.85	0.91	0.95

cm^3/g, respectively. These results are confirmed by Tsai *et al.*, (2006). Fig. 2, shows that although increasing of the ES dose led to increasing of dye removal efficiency but resulted in decreasing of adsorbed dye per mass unit of ES. This result may be related to occupation patterns of active sites and may be in higher doses of ES, 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). Fig.3, shows in the same contact time, increasing of RR123 dye concentration led to increasing of q_e (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 ES surface (Hameed and Ahmad, 2009).

Also, Fig. 3 represents that vacant sites on Es surface has the key role on pollutant adsorption so, in preliminary steps of contact time, the adsorption rate of dye is higher and the lapse time leads to reducing of this rate, because in progressed contact time, the remaining vacant sites are difficult to be occupied due to repulsive forces between the molecules of the ES surface and the aqueous solution (Mezenner and Bonsmaili , 2009). As shown in Fig. 3 the adsorption of RR123 onto ES reached to equilibrium after 120 min that complies with Tsai *et al.*, (2008 b) results. (Tsai *et al.*, 2008 b). Fig. 4 shows the effect of pH on RR 123 dye removal within ES. This result may be related to ionization degree of dye molecules and relevance functional groups of ES surface (Zheng *et al.*, 2007). Also, this phenomenon may be related to electrostatic interactions which appear between positive and negative charges of RR 123 species and adsorbent surface (Bilgiç., 2005 ; Medelline-castillo *et al.*, 2007).

Fig.5 that shows the elevation of the solution temperature from 15°C to 45°C led to increasing of q_e from 0.3 mg/g to 0.6 mg/g. This phenomenon revealed that elevation of solution temperature increases the dye molecules mobility and number of molecules that acquire sufficient energy to undergo an interaction with ES surface (Hameed *et al.*, 2007). This observation was similar to other researches reported (Tsai *et al.*, 2008 b).

Furthermore increasing of temperature may lead to swelling effect in internal surface of the ES enabling large quantities of RR 123 dye to penetrate further onto ES structure.

Table 2 revealed that the adsorption of RR123 dye onto ES can be described with the Langmuir and Freundlich isotherms. These findings are in accordance with Zhang *et al.*,(2007) results. The similarity of these results may be related to adsorbent characteristics especially in term of chemical constituents. Tsai *et al.*, (2008 b) reported that the adsorption of Methylene blue within ES was well fitted with Freundlich isotherm model. Although the findings of this experimental study is not in accordance with Tsai *et al.*,(2008 b) results but survey of the correlation coefficients of adsorption models which were reported by these researchers show that the differences between these coefficients are not significant and can be ignored ($R^2=0.9$ for Langmuir model vs. 0.94 for Freundlich model). Table 3 represents that the adsorption of RR 123 onto ES was well fitted with pseudo-second-order kinetic ($R^2= 0.99$). Tsai *et al.*,(2008 b) studied the adsorption kinetic of cationic basic blue, and anionic acidic orange 51 onto calcified eggshell and ground eggshell powder and reported that the adsorption of these dyes in these adsorbents complies with pseudo-second order kinetics (Tsai *et al.*, 2008 b). Based on these findings it is shown that although the adsorbate specificities have a key role in adsorption kinetic characteristics, but in adsorption studies that ES was used as an adsorbent; the adsorbent identification has a predominant role.

ACKNOWLEDGEMENTS

REFERENCES

Aksu, Z., (2005). Application of biosorption for the removal of organic pollutants: a review, Process Biochem, **40** (3-4): 997-1026.

ASTM., (2007). Test method for partical size distribution of granular activated carbon in: Book of Standard. D2862-

97R04. 26th Edi. Vol. **15**.01, 396-405.

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.

Bilgiç, C., (2005). Investigation of the factors affecting organic cation adsorption on some silicate minerals , J Colloid Interface Sci. **281**: 33-38.

Boer, C.G., Obici, L., Souza, C.G.M., Piralta, R.M., (2004). Decolourization of synthetic dyes by solid state cultures of Lentinula (Lentinus) edodes producing manganese peroxidase as the main lignolytic enzyme, Bioresour. Technol, **94** (2): 107–112.

Choy, K.K.H., and McKay, G., (2005). Sorption of cadmium, copper, and zinc ions onto bone char using Crank diffusion model, Chemosphere. **60**: 1141-1150.

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.

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., and Ahmad, A.A., (2009). Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard. Mater, **164** (2-3): 870-875.

Hameed, B.H., Ahmad, A.A., Aziz, A.N., (2007). Isotherms , kinetics and thermodybamics of acid dye adsorption on activated palm ash. Chem. Eng. J. **133** (1-3) : 195-203.

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

Mahvi, A.H., Ghanbarian, M., Nasseri, S., Khairi., (2009). Mineralization and discoloration of textile wastewater by TiO_2 nanoparticles, Desalination, **239** (1-3): 309-316.

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.*, DOI: 10.1007/s11814-010-0261-0

Medellin-castillo, NA., Leyva-Ramos, R., Ocampo-Perez, R., Garcia de la Cruz, R.F., Aragon-Pina, A., Martinez-Rosales, J.M., (2007). Adsorption of fluoride from water solution on bone char, Ind. Eng. Chem. Res. **46** (26): 9205-9212.

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.

Netpradita, S., Thiravetyan, P., Towprayoon, S., (2004). Adsorption of three azo reactive by metal hydroxide sludge: effect of temperature, pH and electrolytes, J. Colloid Interface Sci, **270** (2): 255–261.

Orfão, J.J., Silva, A.I., Pereira, J.C., Barata, S.A., Fonseca,

I.M., Faria, P.C., Pereira, M.F., (2006). Adsorption of a reactive dye on chemically modified activated carbons--influence of pH, J. Colloid Interface Sci, **296** (2): 480-489.

Purevsuren, B., Avid, B., Narangerel, J., Gerellama, T., Davaajav, Y.A., (2004). Investigation on the pyrolysis products from animal bone, J. Mater. Sci, **39** (2): 737-740.

Rezaee, A., Ghaneian, M.T., Khavanin, A., Hashemian, S.J., Moussavi, Gh., Ghanizadeh, Gh., Hajizadeh, E., (2008). Photochemical oxidation of reactive blue 19 dye (RB19) in textile wastewater by $UV/K_2S_2O_8$ process, Iran. J. Environ. Health. Sci. Eng. **5** (2): 95-100.

Rezaee, A., Ghanizadeh, Gh., Behzadiyannejad, G., Yazdanbakhsh, A., Siyadat, S.D., (2009). Adsorption of endotoxin from aqueous solution using Bone Charcoal, Bull Environ. Contam. Toxicol, **82** (6): 732-737.

Sariglu, M., and Aatay, U.A., (2006). Removal of methylene blue by using biosolid, J. Global Nest, **8** (2): 113-120.

Shieldes, J.E., Thomas, M.A., Thommes, M., (2004). Characterization of porous solids and powders: Surface area, pore size and density. Netherland, Kluwer Acamic Publishers, 58-63.

Tsai, WT., Yang, JM., Lai, CW., Cheng, YH., Lin, CC., Yeh, CW.,(2006). Characterization and adsorption properties of eggshells and eggshells membrane. Bioresor Technol. **97**: 488-493.

Tsai, W.T., Yang, J.M., Hsu, H.C., Lin, C.M., Lin, K.Y., Chiu, C.H., (2008a). Development and characterization of mesoporosity in eggshell ground by planetary ball milling, Microporous and Mesoporous Materials, **111** (1-3): 379–386.

Tsai, W.T., Hsien, K.J., Hsu, H.C., Lin, K.Y., Chiu, C.H., (2008b). Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresor. Technol. **99** (6): 1623-1629.

Vágvölgyi, V., Kovács, J., Horváth, E., Kristóf, J., Makó, É., (2008). Investigation of mechanochemically modified kaolinite surfaces by thermoanalytical and spectroscopic methods, J. Colloid. Interface. Sci, **317** (2): 523-529.

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.

Yu, J.X., Sun, Li, B.H., Sun, X.M., Jun, Y., Chi, R., (2009). Adsorption of methylene blue and rhodamine B on baker's yeast and photocatalytic regeneration of the biosorbent, Biochem Eng. J, **45** (2): 145-151.

Zheng, W., Li, X.M., Yang, Q., Zeng, G., Shen, X., Zhang, Y., Liu, J., (2007). Adsorption of Cd (II) and Cu (II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste. J. Hazard Mater. **147** (1-2): 534-539.