International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1532-1540, April-June 2013

Adsorption Of Congo Red From Aqueous Solution Using Powdered Eggshell

Muhammad Ali Zulfikar* and Henry Setiyanto

Analytical Chemistry Research Group, Institut Teknologi Bandung, Jl. Ganesa 10 Bandung 40132, Indonesia.

***Corres.author: zulfikar@chem.itb.ac.id**
Tel.: +62-22-2502103; Fax: +62-22-2504154.

Abstract: The adsorption of congo red (CR) from aqueous solution using untreated powdered eggshell by varying the parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature was investigated. Adsorption isotherms of CR onto powdered eggshell were analyzed by Langmuir, Freundlich and Sips models. It was observed that the optimum CR adsorption onto powdered eggshell occurred at contact time of 20 minutes, the adsorbent dosage of 20 g, initial concentration of 20 mg/L and pH 2. In addition, the particle size of powdered eggshell has no significant effect on the adsorption of CR. Adsorption isotherms studied through the use of graphical methods revealed that the adsorption of CR onto powdered eggshell follows the Langmuir model, with the maximum adsorption capacity was 95.25 mg g^{-1}. The powdered eggshell investigated in this study thus exhibited as a high potential adsorbent for the removal of CR from aqueous solution.
Keywords: adsorption; congo red; dye; eggshell; isotherm.

Introduction

One of the major problems concerning textile, rubber, paper, paints, printing inks, food and plastic industrial wastewater is colored effluent. In the textile industry, the main sources of wastewater are the dyeing and finishing operations. The wastewater thus generated contains a wide range of contaminants such as salts, dyes, enzymes, yeasts, surfactants, scouring agents, oil, grease, oxidizing and reducing agents[1]. These make treatment of this wastewater more difficult. Further, discharging even small amount colored wastewater is not only damaging the aesthetic nature of receiving streams, but also it can affect aquatic life and food webs due to the carcinogenic and mutagenic effects of synthetic dyes [2,3].

Synthetic dyes as congo red (CR) are difficult to biodegrade due to their complex aromatic structures, which provide them physico-chemical, thermal and optical stability [3,4].

Physical and chemical processes to remove color and toxicity from wastewater were extensively studied. These processes include ion exchange, coagulation, flotation, oxidation, biosorption, biodegradation, UV photodecomposition and reverse osmosis. Most of these processes are high energy consumption or expensive and none of them are considered commercially. Therefore, there is an urgent requirement for development of low cost processes, by which dye molecules can be removed.

Adsorption has been found to be an efficient and inexpensive method for removal dyes, pigments and other colorants and for controlling the bio-chemical oxygen demand. Activated carbon, inorganic oxides, mineral and natural adsorbents have been extensively used as adsorbents to treat wastewater[5,6]. Activated carbon is the most popular adsorbent for removal of dyestuff from wastewater[7]. However, there problems are associated with the use of carbon for the adsorption of pollutants: its relatively high cost, regeneration and reuse are difficult, and it is limited to the removal of non-polar materials[8]. Therefore, there is a need to find locally available, low cost and effective materials for dyes wastewater treatment.

In recent years, numerous low cost natural materials such as phyrophyllite[1], rice husk[4], montmorillonite[7], plant[9], activated carbon prepared from coir pith[10], bagasse[11], fungi[12], soil [13], clay mineral[14,15,16], fruit shell[17], water hyacinth root[18], activated carbon prepared from algae[19], chitosan hydrogel[20] and other adsorbents[3,21] have been used and investigated for removal and adsorption of CR from aqueous solution.

Meanwhile, eggshells are used in enormous quantities by food manufacturers, restaurants and household and the shells are disposed of as solid waste. Investigations have been conducted to explore the possibility of useful applications of eggshells, especially for wastewater. Research has shown that eggshells and eggshell membrane may be used as an adsorbent for iron[22], cadmium[23,24], chromium[23,25-28], lead[23,29], arsenic[8], reactive dye[30-32], cationic dye[33], azo dye[34], malathion[35], lignosulfonate[36] and humic acid from peat water[37]. However, there has so far been no study reported in academic literature related to the use of powdered eggshells as an adsorbent for removing CR from aqueous solution. Therefore the main aim of this study was the use of powdered eggshells as adsorbent material for removal of CR from aqueous solution. The effects of agitation time, dye concentration, adsorbent dose, pH and temperature on the adsorption of CR were investigated.

Materials and Methods

Materials

Chicken eggshells were collected from local restaurants in Bandung, Indonesia. The membranes were separated from the eggshells by hand. The eggshells were then washed with distilled water, air-dried, ground into powder with particle sizes of 100 µm and finally dried at 105 ^{o}C in an oven for 2 h. The characteristics of the eggshells are showed at[36,37]. Sodium hydroxide and hydrochloric acid used to adjust pH was purchased from Merck. Congo red, an azo dye was obtained from Merck was used as adsorbate. All materials were used without further purification.

Methods

Sorption studies

Adsorption experiments were carried out by agitating 5 g of adsorbent with 50 ml of CR solution of the desired concentration and pH at 200 rpm, 25 ^{o}C in a thermostated rotary shaker (ORBITEK, Chennai, India) for 2, 5, 10, 15, 20, 25, 30, 45, 60, 75 and 90 minutes. Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 495.7 nm using a UV-vis spectrophotometer (Hitachi, model U-3210, Tokyo). pH was measured using a pH meter (300 Hanna Instrument, USA). The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 20.000 rpm for 10 min. The absorbance of supernatant solution was measured. The effect of pH on the adsorption of CR compounds was studied by conducting equilibrium sorption tests at different suspension pH values (2.0-10.0) using 5 g of powdered eggshell for 5, 10, 15, 30, 45, 60, 75, and 90 minutes. The suspension pH was adjusted by using dilute NaOH and HCl solutions. Effect of adsorbent dosage was studied with different adsorbent doses (5, 10, 15 and 20) and 50 ml of 20 mg/L CR solutions at equilibrium time and pH 7. The effect of particle size was investigated by using three different particle size: 50, 100 and 150 µm, of powdered chicken eggshells. The experiments were carried out using 20 g of powdered eggshell for 60 minutes. Langmuir, Freundlich and Sips isotherms were employed to study the adsorption capacity of the adsorbent.

Desorption studies

The adsorbent that was used for the adsorption of 20 mg/L of CR solution was separated from the dye solution by centrifugation. The dye loaded adsorbent was filtered using Whatman filter paper and washed gently with water to remove any unadsorbed dye. The powdered eggshell was then loaded with 50 mL of HCl at concentration 0.1 to 0.001 M for 90 minutes. The desorption percentage (DP) of humic acid is defined as [36,38]:

$$DP = \frac{C_{e(des)}}{C_{e(ads)}} \text{ x } 100\% \qquad (1)$$

Results and Discussion

Effect of agitation time and concentration of dye on sorption process

Effects of agitation time on removal of CR by powdered eggshell for different CR concentrations are presented in Figure 1. The percent removal of dye increased with increase in agitation time and reached equilibrium after 20 min for the dye concentrations used in this study.

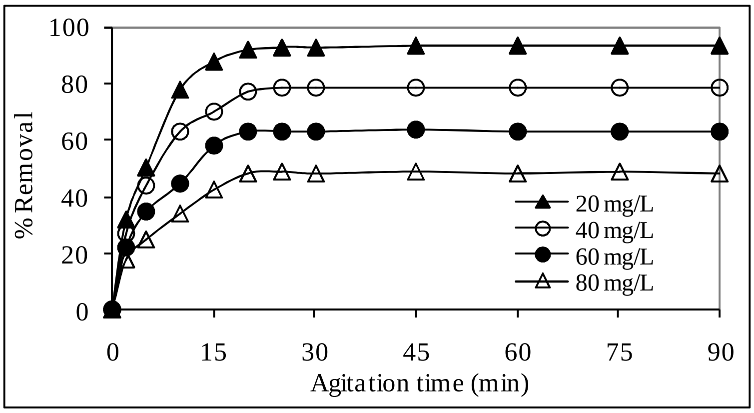

Fig. 1. Effect of agitation time and concentration of dye on CR removal.

The percent CR removal at equilibrium decreased from 93 to 48.5 as the dye concentration was increased from 20 to 80 mg/L. This is due to increase in the initial concentration provides an important driving force to overcome all resistances of the dye between the aqueous and solid phases[31,32,39]. At lower concentrations, all sorbate ions present in the sorption medium could interact with the binding sites, hence higher percentage removal results. At higher concentrations, because of the saturation of the sorption sites, the percentage removal of the dye shows a decreasing trend[32,40].

Effect of pH on sorption process

Effect of pH on the removal of CR is shown in Figure 2. For 20 mg/L dye concentration the percent removal decreased from 95 to 37, when the pH was increased from 2 to 8 and then the percent removal remained almost the same up to pH 10. The possible mechanisms of adsorption of CR on powdered eggshell may be considered as electrostatic interaction between the protonated surface of powdered eggshell and dye. The decrease of CR removal may be related to the formation of negative surface charges of powdered eggshell at higher pH. Our study previously shows that the zero point of charge (pH_{PZC}) of powdered eggshell was at pH = 8.8 [37]. At pH < pH_{PZC}, the surface becomes positively charged, and favors uptake of dye due to increased electrostatic force of attraction. At the solution having pH > pH_{PZC}, the adsorbent surface becomes negatively charge and does not favors the adsorption of dye anions due to the electrostatic repulsion. The results show that the dye removal decrease with increasing initial pH of the dye solution and maximum removal occurs at pH 2.

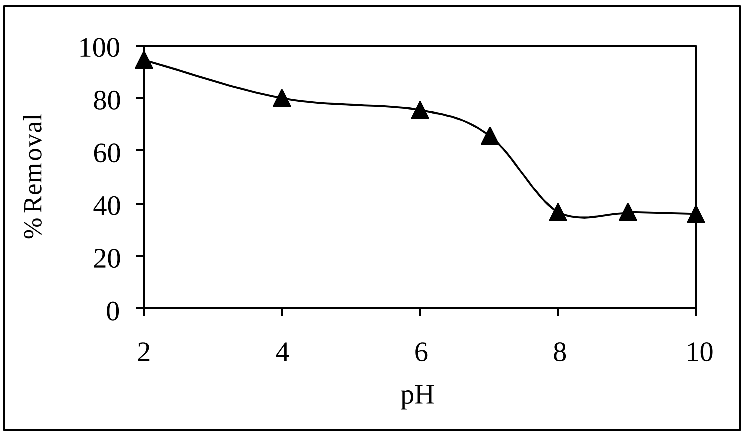

Fig. 2. Effect of pH solution on CR removal.

Effect of particle size of powdered eggshells on sorption process

Determination of the effect of particle size on sorption was conducted using samples of three different average particle sizes: 50, 100 and 150 μm at pH 2 and temperature of 25 ^oC for 90 minutes. The result is shown at Figure 3. As seen from Figure 3, variation of the particle size of powdered eggshells statisticaly has no significant effect on the removal of CR compounds as indicated by 86 - 91%.

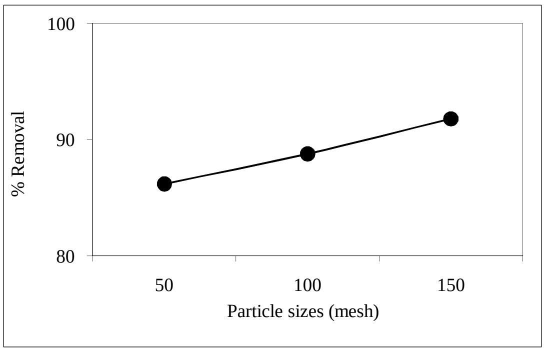

Fig. 3. Effect of particle size of powdered eggshells on CR removal.

Effect of powdered eggshells dosage on sorption process

Figure 4 shows the removal of CR by powdered eggshell at different adsorbent doses (5-30 g) for the dye concentrations of 20 mg/L at pH 2. Increase in adsorbent dosage increased the percent removal of dye, which is due to the increase in absorbent surface area of the adsorbent.

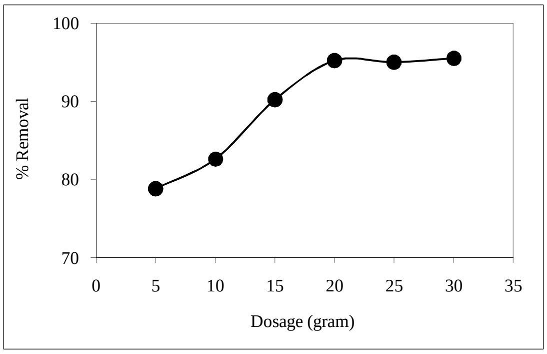

Fig. 4. Effect of powdered eggshells dosage on CR removal.

Adsorption isoterm

Langmuir isotherm is represented by the following equation below:

$$q_e = \frac{q_m.b.C_e}{1+b.C_e} \qquad (2)$$

where q_e and q_m is the amount adsorbed at equilibrium and maximum mg/g, respectively, C_e is the equilibrium concentration (mg/L) and b is the Langmuir isotherm constant (L/mg). The plot of q_e vs C_e is shown in Figure 5. Values of Langmuir constants are tabulated in Table 1. From Figure 5, we can see that the adsorption curves were single, smooth, plateau, continuous, leading to saturation, and this indicates the possible monolayer coverage on the surface of the adsorbent [41]. From the linearization plot of the Langmuir isotherm model, the value of q_m in our experiment was found to be 95.25 mg/g.

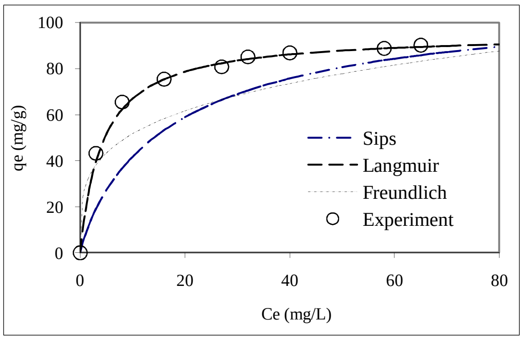

Fig. 5. Non-linear isotherm of CR adsorption onto powdered eggshell.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by [3,9,14,16,20,42,43]:

$$R_L = \frac{1}{1 + aCo} \tag{3}$$

Which a (or b) is Langmuir constant and C_o is initial dye concentration (mg/L). The R_L value indicates the isotherm shape according to the following adsorption characteristics: $R_L > 1$ (unfavorable), $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible) and $0 < R_L < 1$ (favorable) [3,9,14,16,20,42,44]. The value of R_L in this study was found 0.18. This suggests that adsorption of CR by powdered eggshell is favorable.

Table 1. Langmuir, Freundlich and Sips constants for CR adsorption

Langmuir Model			Freundlich Model			Sips Model			
b (L/mg)	q_m (mg/g)	R^2	n	K_f (mg/g)	R^2	q_m (mg/g)	K_{eq} (mL/g)	n	R^2
0.236	95.25	0.999	3.93	28.8	0.957	90.3	0.095	0.898	0.981

The Freundlich isotherm was also applied for the adsorption of CR onto powdered eggshell by using the equation below:

$$q_e = K_f C_e^{\ 1/n} \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of absorbent (mg/g), K_f and n is Freundlich constants.

Plots of q_e vs C_e for the dye concentrations of 20 mg/L show that the adsorption could not be fitted by this model (Fig. 5) and hence the adsorption does not follow the Freundlich isotherm at these concentrations. Values of K_f and n are presented in Table 1.

Sips model is a three-parameter isotherm model that is basically a combination of Langmuir and Freundlich models. It is expressed as:

$$q_e = \frac{q_m.K_{eq}.C_e{}^n}{1+K_{eq}.C_e{}^n} \tag{5}$$

where K_{eq} (L/mg) represents the equilibrium constant of the Sips equation and q_m (mg/g) is the maximum adsorption capacity. The Sips isotherm model is characterized by the heterogeneity factor, n, and specifically when n = 1, the Sips isotherm equation reduces to the Langmuir equation and it implies a homogenous adsorption process [3,20,21].

The value of the heterogeneity factor (n) of powdered eggshell is 0.864 and this indicates a homogenous adsorption process (Table 1). The maximum adsorption capacity of chitosan-silica beads obtained from the Sips isotherm was 90.3 mg/g.

In our experimental range, the results of powdered eggshells are best described using the Langmuir model, as indicated by the well fitted curve lines.

Desorption study

Desorption study will help to elucidate the nature of adsorption process and recycling of the spent adsorbent and the dye [9,14]. One of the important characteristics of an adsorbent is its ability to be regenerated [38]. The most common desorbing agents used to desorbs adsorbates are NaOH, HCl, HNO_3, EDTA, $CaCl_2$ and organic solvents such as methanol and ethanol [38]. In this study only HCl was used to regenerate the adsorbent. The results for desorption studies found that the maximum desorption percentage of CR was achieved by treating powdered eggshell with 1.0 M HCl (Figure not shown). This could be due to the increased solubility of CR in acidic medium [9].

Comparison of lignosulfonate adsorption with other adsorbents reported in the literature

Several studies have been investigated on removal of CR in aqueous solution using low cost adsorbents. Table 2 summarises the adsorption capacity of different types of adsorbents for CR removal. It can be seen that adsorption capacity varies and depends on the properties of the individual adsorbent, the extent of surface/surface modification, the initial concentration of the adsorbate [16,45], range of molecular size fraction of adsorbate and degree of ionization per unit weight of adsorbate [46].

Table 2. Comparison of adsorption capacity of various adsorbent for CR removal

Adsorbent	q_m (mg/g)	Reference
Phyrophyllite	4.00	1
Chitosan hydrogel beads impregnated with CTAB	433.12	3
Surfactant-modified montmorillonite	351.0	7
Alternanthera bettzichiana plant powder	14.67	9
Activated carbon prepared from choir pith	6.72	10
Sugarcane bagasse	38.20	11
Mycelial pellets of *Trametes versicolor*	51.81	12
Soil (30 ^{o}C)	8.65	13
Organo-attapulgite	189.39	14
Burnt clay	22.86	15
Kaolin	5.44	16
Tamarind fruit shell	10.48	17
Water hyacinth roots	13.46	18
Carbon prepared from algae *Valoria bryopsis*	20.20	19
Chitosan hidrogel bead-SDS	186.02	20
Chitosan hydrogel beads impregnated with carbon nanotubes	450.40	21
Powdered eggshell	95.25	This study

Conclusions

In this study, the adsorption of CR on powdered eggshell under the influences of contact time, initial concentration, particle size of adsorbent, adsorbent dosage and pH were investigated. The optimum CR adsorption onto powdered eggshell occurred at contact time of 20 minutes, the adsorbent dosage of 20 g, initial concentration of 20 mg/L and pH 2. The particle size of powdered eggshell has no significant effect on the adsorption of CR. Adsorption isotherms studied shows that the adsorption of CR onto powdered eggshell follows the Langmuir model, with the maximum adsorption capacity was 95.25 mg g^{-1}. The desorption of CR from powdered eggshell could be obtained by using HCl 0.1 M.

Acknowledgments

The authors wish to extend their gratitude Institut Teknologi Bandung for their financial support throughout this research.

References

1. Amran, M.B. and Zulfikar, M.A., Removal of Congo Red dye by adsorption onto phyrophyllite, International Journal of Environmental Studies, 2010, 67(6), 911-921.
2. Crini, G., Non-conventional low-cost adsorbents for dye removal: a review, Bioresource Technology, 2006, 97, 1061-1085.
3. Chatterjee, S., Lee, D.S., Lee, M.W. and Woo, S.H., Enhance adsorption of congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide, Bioresource Technology, 2009, 100, 2803-2809.
4. Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y. and Zou, L., Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Bioresource Technology, 2008, 99, 2938-2946.
5. Al-Asheh, S., Banat, F. and Aitah, L.A., Adsorption of Phenol Using Different Types of Activated Bentonites, Separation and Purification Technology, 2003, 33, 1-10.
6. Naseem, R. and Tahir, S.S., Removal of Pb (II) From Aqueous/ Acidic Solutions by Using Bentonite as an Adsorbent, Water Research, 2001, 35 (16), 3982-3986.
7. Wang, L. and Wang, A., Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorillonite, Journal of Hazardous Materials, 2008, 160, 173-180.
8. Oke, I.A., Olarinoye, N.O. and Adewusi, S.R.A., Adsorption kinetics for arsenic removal from aqueous solutions by untreated powdered eggshell, Adsorption, 2008, 14, 73-83.
9. Patil, A.K. and Shrivastava, V.S., *Alternanthera bettzichiana* plant powder as low cost adsorbent for removal of Congo red from aqueous solution, International Journal of ChemTech Research, 2010, 2 (2), 842-850.
10. Namasivayam, C. and Kavitha, D., Removal of Congo Red from water by adsorption onto activated carbon prepared from choir pith, an agricultural solid waste, Dyes and Pigments, 2002, 54, 47-58.
11. Zhang, Z., Moghaddam, L., O’Hara, I.M. and Doherty, W.O.S., Congo Red adsorption by ball-milled sugarcane bagasse, Chemical Engineering Journal, 2011, 178, 122-128.
12. Binupriya, A.R., Sathishkumar, M., Swaminathan, K., Ku, C.S. and Yun, S.E., Comparative studies of removal of Congo red by native and modified mycelial pellets of *Trametes versicolor* in various reactor modes, Bioresource Technology, 2008, 99, 1080-1088.
13. Smaranda, C., Gavrilescu, M. and Bulgariu, D., Studies on sorption of Congo red from aqueous solution onto soil, International Journal of Environmental Research, 2011, 5 (1), 177-188.
14. Chen, H. and Zhao, J., Adsorption study for removal of Congo red anionic dye using organo-attapulgite, Adsorption, 2009, 15, 381-389.
15. Mumin, M.A., Khan, M.M.R., Akhter, K.F. and Uddin, M.J., Potentially of open burnt clay as an adsorbent for the removal of Congo red from aqueous solution, International Journal of Environmental Science and Technology, 2007, 4 (4), 525-532.

16. Vimonses, V., Lei, S., Jin, B., Chow, C.W.K. and Saint, C., Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay minerals, Chemical Engineering Journal, 2009, 148, 354-364.
17. Reddy, M.C.S., Removal of direct dye from aqueous solutions with an adsorbent made from tamarind fruit shell, an agricultural solid waste, Journal of Scientific and Industrial Research, 2006, 65, 443-446.
18. Rajamohan, N., Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots, African Journal of Environmental Science and Technology, 2009, 3 (11), 399-404.
19. Jayaraj, R., Thanaraj, P.J., Natarajan, S.T. and Prasath, P.M.D., Removal of Congo red dye from aqueous solution using acid activated eco-friendly low cost carbon prepared from marine algae *Valoria bryopsis*, Journal of Chemical and Pharmaceutical Research, 2011, 3 (3), 389-396.
20. Chatterjee, S., Chatterjee, T. and Woo, S.H., Adsorption of Congo Red from aqueous solution using chitosan hydrogel beads formed by various anionic surfactants, Separation Science and Technology, 2011, 46, 986-996.
21. Chatterjee, S., Lee, M.W. and Woo, S.H., Adsorption of congo red by chitosan hydrogel beads impregnated with carbon nanotubes, Bioresource Technology, 2010, 101, 1800-1806.
22. Yeddou, N. and Bensmaili, A., Equilibrium and kinetic modelling of iron adsorption by eggshells in a batch system: effect of temperature, Desalination, 2007, 206, 127-134.
23. Park, H.J., Jeong, S.W., Yang, J.K., Kim, B.G. and Lee, S.M., Removal of heavy metals using waste eggshell, Journal of Environmental Science, 2007, 19, 1436-1441.
24. Kuh, S.E. and Kim, D.S., Removal characteristics of cadmium ion by waste egg shell, Environmental Technology, 2000, 21, 883-890.
25. Chojnacka, K., Biosorption of Cr(III) ions by eggshells, Journal of Hazardous Materials, 2005, 121, 167-173.
26. Ghazy, S.E., El-Asmy, A.A. and El-Nokrashy, A.M., Separation of chromium (III) and chromium (VI) from environmental water samples using eggshell sorbent, Indian Journal of Science and Technology, 2008, 1 (6), 1-7.
27. Rajendran, A. and Mansiya, C., Extraction of chromium from tannery effluents using waste egg shell material as an adsorbent, British Journal of Environment and Climate Change, 2011, 1 (2), 44-52.
28. Liu, B. and Huang, Y., Polyethyleneimine modified eggshell membrane as a novel biosorbent for adsorption and detoxification of Cr (VI) from water, Journal of Materials Chemistry, 2011, 21, 17413-17418.
29. Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P. and Panyawathanakit, P., Removal of lead from battery manufacturing wastewater by eggshell, Songklanakarin Journal of Science and Technology, 2007, 29 (3), 857-868.
30. Pramanpol, N. and Nitayapat, N., Adsorption of reactive dye by eggshell and its membrane, Kasetsart Journal (Natural Science), 2006, 40, 192-197.
31. Ehrampoush, M.H., Ghanizadeh, G. and Ghaneian, M.T., Equilibrium and kinetics study of reactive red 123 dye removal from aqueous solution by adsorption on eggshell, Iran Journal of Environmental Health, Science and Engineering, 2011, 8 (2), 101-108.
32. Elkady, M.F., Ibrahim, A.M. and Abd El-Latif, M.M., Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads, Desalination, 2011, 278, 412-423.
33. Tsai, W.T., Yang, J.M., Lai, C.W., Cheng, Y.H., Lin, C.C. and Yeh, C.W., Characterization and adsorption properties of eggshells and eggshell membrane, Bioresource Technology, 2006, 97, 488-493.
34. Tao, L., Treatment of model wastewater including Eriochrome Black T based on eggshell membrane, Advance Materials Research, 2011, 183-185, 2120-2123.
35. Elwakeel, K.Z. and Yousif, A.M., Adsorption of malathion on thermally treated eggshell material, Proceeding of 14^{th} International Water Technology Conference, 2010, Cairo, Egypt, 53-65.
36. Zulfikar, M.A., Mariske, E.D. and Djajanti, S.D., Adsorption of lignosulfonate compound using powdered eggshells, Songklanakarin Journal of Science and Technology, 2012, 34 (3), 309-316.

37. Zulfikar, M.A., Novita, E., Hertadi, R. and Djajanti, S.D., Removal of humic acid from peat water using untreated powdered eggshell as a low cost adsorbent, submitted to International Journal of Environmental Science and Technology, 2013.
38. Ngah, W.S.W., Hanafiah, M.A.K.M. and Yong, S.S., Adsorption of humic acid from aqueous solutions on crosslinked chitosan-epichlorohydrin beads: Kinetics and isotherm studies, Colloids Surface B, 2008, 65, 18-24.
39. Kumar, P.S., Vincent, C., Kirthika, K. and Kumar, K.S., Kinetics and equilibrium studies of Pb^{2+} ion removal from aqueous solutions by use of nano-silver sol-coated activated carbon, Brazilian Journal of Chemical Engineering, 2010, 27 (2), 339-346.
40. Aravindhan, R., Fathima, N.N., Rao, J.R. and Nair, B.U., Equilibrium and thermodynamic studies on the removal of basic black dye using calcium alginate beads, Colloids and Surface A, 2007, 299, 232-238.
41. Ratinac, K.R., Standard, O.C. and Bryant, P.J., Lignosulfonate adsorption on and stabilization of lead zirconate titanate in aqueous suspension, Journal of Colloid and Interface Science, 2004, 273, 442-454.
42. Choi, Y.S. and Cho, J.H., Color removal from dye wastewater using vermiculite, Environmental Technology, 1996, 17, 1169-1180.
43. Lin, S.H. and Huang, R.S., Heavy metal removal from water by sorption using surfactant-modified montmorillonite, Journal of Hazardous Materials B, 2002, 92, 315-326.
44. Mamdouth, N.N., Kamar, T.E., Ebrahiem, E.E., Yehia, H.M. and Mansour, H.M., Adsorption of iron and manganese ions using low cost materials as adsorbents, Adsorption Science and Technology, 2004, 22 (1), 25-37.
45. Mousavi, H.Z. and Seyedi, S.R., Nettle ash as a low cost adsorbent for the removal of nickel and cadmium from wastewater, International Journal of Environmental Science and Technology, 2011, 8 (1), 195-202.
46. Garcı´a, M.A.F., Utrilla, J.R., Toledo, I.B. and Castilla, C.M., Adsorption of humic substances on activated carbon from aqueous solutions and their effect on the removal of Cr (III) ions, Langmuir, 1998, 14, 1880-1886.

*****