Adsorption of a di-azo aromatic dye from the aqueous environment by eggshell: Isotherm and kinetic study

Soma Mukherjee
Department of Environmental Science, University of Kalyani,
Kalyani, Nadia – 741235, West Bengal, India

Hemanta Mukherjee
Department of Environmental Science, University of Kalyani,
Kalyani, Nadia – 741235, West Bengal, India

Abstract- Eggshell along with its modified and engineered forms act as green adsorbents which have the potentiality to decontaminate water and wastewater from toxic ions, dyes, pigments and other emerging pollutants. The present study states that the aromatic dye with the di-azo group, *viz*. Bismarck Brown (BB) is strongly adsorbed by eggshell and its ash (ES-75, AES-75; Size 75- micron). The isotherm models (Freundlich isotherm) and surface morphologies using scanning electron microscopy (SEM) indicated that both ES-75 and AES-75 are heterogeneous in nature. Pseudo-second-order kinetic models are found to fit well for both adsorbents (ES-75 and AES-75). The absorptive optimization has also been studied under varied conditions of several parameters (pH, dose, contact time and initial concentration).

Keywords – Eggshell, Isotherm, Surface morphology, Pseudo-second-order kinetics.

I. INTRODUCTION

Water contaminated with dyestuffs released from various industries exerts a significant impact on the society, as it poses a risk to our ecosystem. Presence of dyes in the aquatic environment affect marine life and diminish the photosynthetic rate by obstructing the sun light penetration. Also, it raises the chemical oxygen demand and entered into the food web in the long run [1]. Several technologies are available for removal of dyes like oxidation, precipitation, coagulation, electro-coagulation, adsorption, ion exchange, membrane separation, biological treatment etc. [2-4]. Among them, the adsorption process is widely applicable due to its universal nature, inexpensiveness, removal efficiency as well as ease of operation [5]. Use of low cost and locally available adsorbents from agricultural, industrial and household wastes have gained tremendous attention to the researchers for treatment of the wastewater. In recent years, waste biomass has been effectively applied for removal of several pollutants from the aqueous phase [6]. In this context, emphasis has been given to explore some natural, renewable, low-cost waste bio-mass as suitable green adsorbents for the decontamination of wastewater [7]. Eggshell is one of such waste bio-mass which has high porosity and approximately 11% of the total egg weight [8].
The present work has been performed to explore the adsorption potential of waste eggshell for the removal of a di-azo cationic dye (Bismarck brown) from the aqueous environment. The effect of several parameters, *viz.* dosages of adsorbent, time of contact, pH and initial dye concentration during adsorption have also been investigated. The adsorption efficiency of eggshell has been studied by several researchers for removal of heavy metals, anions, dyes and pigments, emerging contaminants etc. [9].

II. MATERIALS AND METHODS

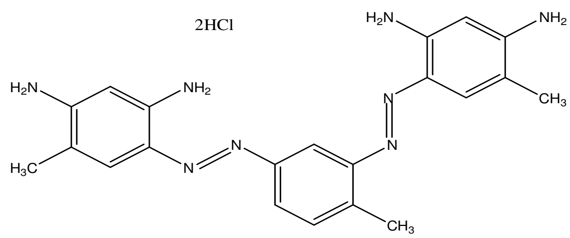
2.1 Preparation of adsorbents –

The waste eggshell has been collected from hostels, canteens, fast-food shops and cleaned to remove impurities. Further it is boiled for 30 min to separate the membrane. The eggshell is crushed with the help of a mortar pestle, sieved to 75 microns and coded as ES-75. Then, ES-75 is kept in the muffle furnace at 850 ℃ for 120 min and allowed to cool at the room temperature. The ash of ES-75 is coded as AES-75 for further use.

The morphologies of ES-75 and AES-75 have been studied after gold coating by the scanning electron microscope (SEM) (DSM-942, Zeiss, Germany). Fourier transform infrared (Shimadzu FTIR 8400) analysis is carried out to understand the functional groups of both ES-75 and AES-75. X-ray powder diffraction of ES-75 and AES-75 have been also studied (Bruker D8 Advance).

2.2 Preparation of dye –

Bismarck brown, BB (cationic, C21H24N_8.2HCl, CI 21010, λ_{max} 468 nm) dye is used for the adsorption studies. It is supplied by Loba Chemie Pvt. Ltd., Mumbai, India. The stock solutions have been prepared by dissolving 1.0 g of dye in 1000 ml of double-distilled water. All working standard solutions have been prepared by diluting the stock solution with the double distilled water.



Chemical structure of Bismarck brown (BB)

III. Experiment and Result

Equilibrium studies have been carried out in the batch mode with adsorbents (ES-75 and AES-75, 0.01 g) to adsorb BB dye (10 ml) of varied concentrations (100 ppm, 200ppm, 300ppm, 400ppm, 500ppm, 600ppm, 700ppm, 800ppm, 900ppm and 1000 ppm) taken in capped culture tubes (Borosil, 15 ml) and then placed in an orbital shaker (AB-SB systems India) with a constant agitation speed (120 rpm).

The removal percentage of BB (*R %*) from the solution has been calculated by Eq. (1),

$$R(\%) = \frac{C_i - C_e}{C_i} \text{ x } 100\% \qquad \text{Eq. (1)}$$

The amount of BB adsorbed q_t (mg/g) by the adsorbent has been calculated using Eq. (2),

$$q_t = (C_i - C_t) \times \frac{v}{w} \qquad \text{Eq. (2)}$$

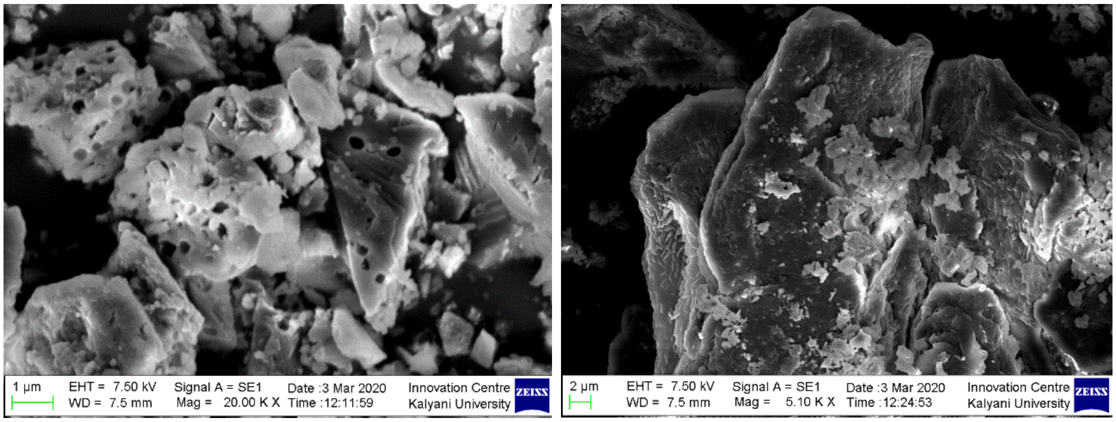
The amount of adsorption at equilibrium, q_e (mg/g), has been calculated by Eq. (3),

$$q_e = [C_i - C_e] \times \frac{v}{w} \qquad \text{Eq. (3)}$$

Where, C_i and C_e represent initial and equilibrium concentrations of the dye respectively (mg/l), C_t is the concentration (mg/l) at time t, V is the volume of the experimental solution (l), and W is the weight of the adsorbent used (g).

3.1 Characterization of materials-

The surface morphologies of ES-75 and AES-75 have been studied by scanning electron microscopy (Figure 1a and 1b) operated at 10 kV accelerating potential. It is revealed from the Figure 1 that the surfaces of ES-75 have pores with well-developed cavities and voids. Moreover, the structures of AES-75 exhibit crystallinity and irregular angular pattern of fractures [10]. All structures possess rough, irregular shapes with different sizes.



(a) (b)

Figure 1. SEM image of (a) ES-75 and (b) AES-75

In order to characterize the crystallinity of eggshells, XRD analysis has been performed using Cu Kα radiation beam (λ = 1.5406 $\mathring{A}$), operating at 30 kV and 30 mA with a copper target. Data have been collected between 2θ angles in the range of 10° and 80°. The sizes of three materials have been evaluated using the Scherrer equation, Eq. (4),

$$crystal\ size = \frac{\kappa\lambda}{\beta\cos(\theta)} \qquad \text{Eq. (4)}$$

where, k is Scherrer constant (0.9), λ is wavelength of X-ray (1.5406 $\mathring{A}$ for Cu-Kα), β is full width half maxima, FWHM (radians), θ is angle of diffraction (degree).

Table - 1 Grain size of adsorbents

Sl. No.	**Sample Name**	**2θ (°)**	**θ (°)**	**FWHM (°)**	**FWHM (rad)**	***D* (nm)**
1	**ES-75**	**29.305**	**14.652**	**0.175**	**0.003054675**	**46.923**
2	**AES-75**	**29.218**	**14.609**	**0.260**	**0.004533842**	**31.614**

The grain sizes of three consecutive samples have been tabulated in Table 1. The diffractograms indicate that ES-75 and AES-75 (Figure S1) have calcite structures with a similarity to calcium carbonate mineral [11].

The FTIR spectra have been studied (Figure S2) for the characterization of two materials (ES-75 and AES-75). The spectra of ES-75 and AES-75 show characteristic broad peaks ~2920-3384 cm^{-1} corresponding to C-H and O-H bonding vibrations. The stretching vibration at around 1635 cm^{-1} corresponds to amide bond. The peaks at around 1091 cm^{-1}, 943 cm^{-1}, 759 cm^{-1} and 747 cm^{-1} correspond to the Ca-O stretching and may be due to the bending mode of $CaCO_3$ [10, 12-13].

3.2 Influence of experimental parameters on adsorption

Effect of pH

The pH plays a crucial role on the adsorption process. The variation of pH may result in the dissociation of adsorbate species as well as influences the surface chemistry of the adsorbent. Herein, the effect of pH on the BB dye adsorption (50 mg/g, 10 ml distilled water) has been investigated at different pH values (3 - 10) with 120 min shaking in an orbital shaker at 120 rpm. Above pH 10, there may be the possibility of the dissolution of $CaCO_3$ present in the egg shell. The removal percentages (% R) are highest at pH 5 for both adsorbents (96.4% for ES-75, 95.9% for AES-75) (Figure 2), which indicate that the protonation of BB possibly facilitates the adsorption process [4].

Effect of contact time

In order to establish the equilibration time for maximum uptake of BB (50 ppm), the effect of contact time has been studied using ES-75 and AES-75 (10 mg) with constant shaking (120 rpm). It is found that the percentages of removal of BB dye by ES-75 and AES-75 have been increased (88% - 93%) with time (30 min - 180 min) (Figure

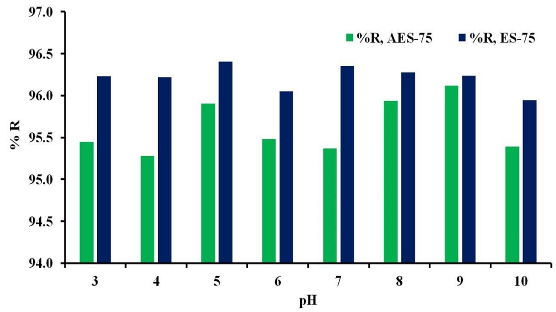
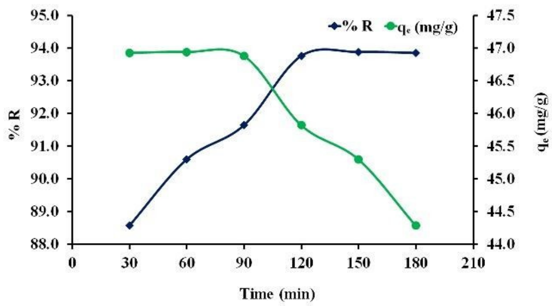


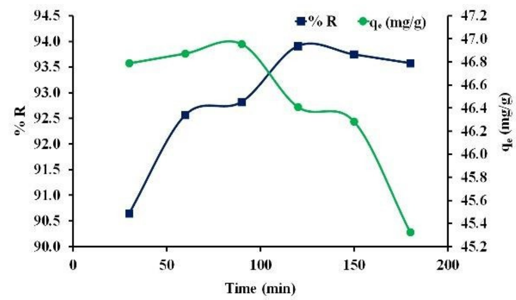
Figure 2. Effect of pH on dye adsoprtion

3a and 3b) and reached maximum, 93.7% (ES-75) and 93.9% (AES-75), at 120 min indicating the optimum contact time for highest uptake capacities (45.82 mg/g for ES-75, 46.4 mg/g for AES-75).

Initially, large number of vacant sites are available on the surface of adsorbents which is responsible for the rapid removal of the dye [14]. Later the adsorption process becomes slow due to the decrease of available vacant sites of adsorbents as well as increase in the repulsive forces between dye molecules adsorbed onto the surface of ES-75 and AES-75 in the aqueous phase.



(a)



(b)

Figure 3. Effect of contact time on adsorption of dye by (a) ES-75 and (b) AES-75

Effect of initial concentration of dye

The effect of the initial concentration of BB dye (50 ppm - 1000 ppm, 10 ml of distilled water) on adsorption has been studied by the batch mode with fixed ES-75 and AES-75 (0.01 g) dosages for 90 min constant shaking in an orbital shaker (Figure 4a). The adsorption uptake (q_e) values of ES-75 and AES-75 increase at equilibrium from 46.2 mg/g to 957.27 mg/g and 45.75 mg/g to 955.68 mg/g respectively. The above experiment also states that the uptake capacity increases linearly with the increase of initial dye concentration which resembles the early work of J. Mittal [15].

Effect of adsorbent dosages

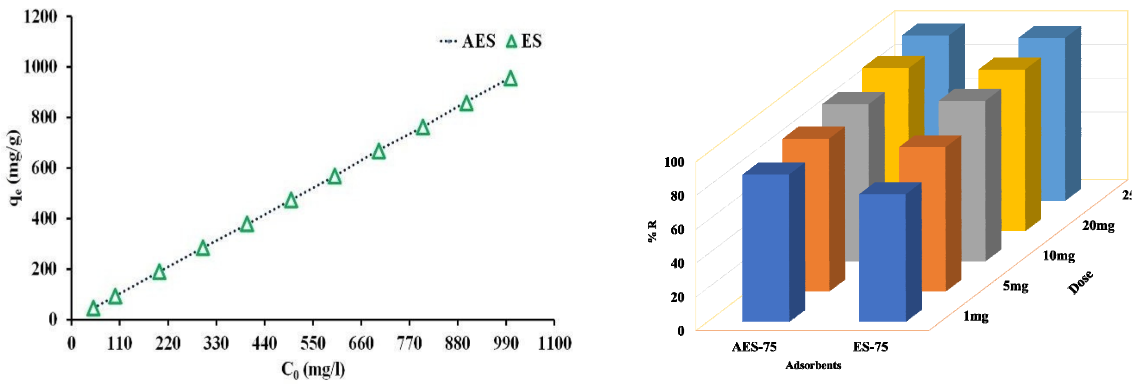
The dose of adsorbents, ES-75 and AES-75, are also very important to evaluate the removal efficiency of BB dye from the aqueous environment. In order to study the influence of dosages of ES-75 and AES-75 on adsorption, the amounts of each adsorbent are varied from 1 mg to 25 mg (1 mg, 5 mg, 10 mg, 20 mg, 25 mg).

Interestingly, the removal efficiencies of BB dye have been increased from 75.27% to 96.29% for ES-75 and 86.97% to 97.77% for AES-75 with increasing adsorbent dosages (Figure 4b). Thus, it is clear that the percentage of removal of BB dye increases with the increase of adsorbent dosages till saturation is reached (>10 mg adsorbent) [16].

Kinetic study

The adsorption kinetic study provides idea about the reaction pathways as well as the mechanism of the reaction. Moreover, it gives the necessary information about the adsorbent [17]. In the present work, two equilibrium kinetic models *viz*. pseudo-first-order and pseudo-second-order have been studied [18].

It is revealed from the kinetic study that the adsorption uptake capacity increases significantly with the enhancement of contact time and reached saturation with removal percentages of 88.6% for ES-75 and 90.7% for AES-75 at 120 min. The rate of kinetics of BB adsorption on ES-75 and AES-75 follow pseudo-second-order as the linear regression coefficient (R^2 = 0.99) values are highest for both the cases. The rate constants for each system have also been estimated (Table 2).



(a) (b)

Figure 4. (a) Effect of initial concentration of dye (100 ppm – 1000 ppm) (b) Effect of dosages (1 mg – 25 mg) on adsoprtion of dye by ES-75 and AES-75

Table - 2 Parameters of the pseudo-second-order kinetic model

Adsorbents	R^2	q_e	K_2
ES-75	**0.99**	**47.85**	**0.007**
AES-75	**0.99**	**47.62**	**0.01**

** *where,, q_e: amount of dye adsorbed (mg/g) at equilibrium; K_2: second-order reaction rate constant for adsorption (g/(mg·min)).*

Isotherm study

The linear and non-linear isotherm models of Freundlch (using IBM SPSS Statistic 20 software) satisfactorily explained the adsorption phenomena of BB dye on ES-75 and AES-75. The slope of linear plot ranges between 0 to 1 indicated the heterogeneity of the adsorption surfaces. The values of *1/n* are greater than 1 which indicate cooperative adsoprtion. The correlation coefficient (R^2) values are close to unity which reveal the fitness of models.

Table - 3 Isotherm model of adsorption process with parameters and correlation coeffiient

Freundlich isotherm	Adsorbents	Parameters		Std. Error.	R^2
Linear model: $\ln q_e = \ln K_F + (1/n) \ln C_e$	**ES-75**	K_F	**12.516**	**0.087**	**0.995**
		n	**0.886**	**0.027**	
	AES-75	K_F	**9.66**	**0.195**	**0.980**
		n	**0.823**	**0.061**	
Non-linear model: $q_e = K_F{*}C_e^{1/n}$	**ES-75**	K_F	**11.236**	**2.197**	**0.992**
		n	**0.862**	**0.040**	
	AES-75	K_F	**7.965**	**4.150**	**0.951**
		n	**0.785**	**0.091**	

**where K_F and *n* are Freundlich constatnt

Thermodynamic study

The measurement of thermodynamic parameters, Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are very important to define the adsorption process. The parameters can be calculated from binding constant, K, obtained from Langmuir equation [19].

$$\triangle G = -RT \ln K \qquad \text{Eq. (5)}$$

The ΔH values are calculated by Eq. (6) from the slopes of the linear variation of ln K versus 1/T.

$$\ln K = -\triangle H/RT + \text{Constant} \qquad \text{Eq. (6)}$$

The values of ΔS are calculated from Eq. (7)

$$\triangle S = (\triangle H - \triangle G)/T \qquad \text{Eq. (7)}$$

where, R (8.3145 J/mol/Kel) is the ideal gas constant, and T (Kel) is the temperature.

Relevant data calculated from Eqs. (5) – (7) are tabulated in the Table 4. The adsorption of BB increases with the increase of temperature and the values of ΔH are positive which indicate that the absorption process is endothermic and a strong interaction exists between the adsorbent (ES-75 / AES-75) and BB dye. The negative ΔG values at different temperatures reveal that the adsorption process is spontaneous. The decreasing trend of ΔG value with increasing temperature may indicate that the adsorption process is inversely proportional to the temperature. The positive ΔS values further support the affinity of adsorbents (ES-75 and AES-75) towards BB dye.

Table - 4 Thermodynamic parameters for BB dye adsorption on ES-75 and AES-75

ES-75			**AES-75**		
ΔH (KJ/mol)		**18.77**	**ΔH (KJ/mol)**		**28.16**
ΔS (KJ/mol/Kel)		**27.18**	**ΔS (KJ/mol/Kel)**		**60.99**
ΔG (KJ/mol)	**293 Kel**	**-4.45**	**ΔG (KJ/mol)**	**293 Kel**	**-4.11**
	303 Kel	**-4.15**		**303 Kel**	**-4.09**
	313 Kel	**-3.96**		**313 Kel**	**-3.36**

IV.CONCLUSION

The adsorption potential of waste eggshell and its ash has been investigated on a di-azo cationic dye, Bismarck brown, in the aqueous environment. The effects of several parameters (concentration of dye, dose, contact time and pH) on adsoprtion of dye have been studied. FTIR, SEM, XRD techniques have been carried out for the characterization of adsorbents. Both the linear and non-linear Freundlich isotherm models described the adsoprtion process. Kinetic study clearly revealed that the pseudo-second-order is the best fit kinetic model with the highest correlation coefficient value. The thermodynamic analyses indicate the spontaneous and endothermic nature of the dye adsorption process.

REFERENCES

[1] R Sanghi and P. Verma, "Decolorisation of aqueous dye solutions by low-cost adsorbents: a review." Coloration Technology, vol. 129, no. 2, pp. 85-108, 2013.

[2] TK Sen, "Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents," Journal of Chemical and Process Engineering, 2013.

[3] D Mohan, and CU. Pittman. "Arsenic removal from water/wastewater using adsorbents—A critical review." Journal of Hazardous Materials, vol. 142, no. 1-2, pp. 1-53, 2007.

[4] MF Elkady, AM Ibrahim and MM El-Latif. "Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads." Desalination, vol. 278, no. 1-3, pp. 412-423, 2011.

[5] V Gupta, PJ Carrott, MM Ribeiro Carrott and Suhas, "Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review." Critical Reviews in Environmental Science and Technology, vol. 39, no. 10, pp. 783-842, 2009.

[6] E Rapo, K Jakab, K Posta, M Suciu and S Tonk, "A Comparative Study on the Adsorption of Two Remazol Dyes on Green Adsorbent." Revista de Chimie, vol. 71, no. 4, pp. 248-257, 2020.

[7] KY Foo and BH Hameed, "Insights into the modeling of adsorption isotherm systems." Chemical Engineering Journal, vol. 156, no. 1, pp. 2-10, 2010.

[8] KZ Elwakeel and AM Yousif, "Adsorption of malathion on thermally treated egg shell material." Water Science and Technology, vol. 61, no. 4, pp. 1035-1041, 2010.

[9] A Mittal, M Teotia, RK Soni and J Mittal, "Applications of egg shell and egg shell membrane as adsorbents: A review." Journal of Molecular Liquids, vol. 223, pp. 376-387, 2016.

[10] WT Tsai, JM Yang, CW Lai, YH Cheng, CC Lin and CW Yeh, "Characterization and adsorption properties of eggshells and eggshell membrane." Bioresource Technology, vol. 97, no. 3, pp. 488-493, 2006.

[11] FS Murakami, PO Rodrigues, CM Campos and MA Silva, "Physicochemical study of $CaCO_3$ from egg shells." Ciência e Tecnologia de Alimentos, vol. 27, no. 3, pp. 658-662, 2007.

[12] T Oymak and E Bağda, Crosslinked Egg White as Eco-Friendly, "Crosslinked Egg White as Eco-Friendly, Reusable, and Cost-Effective Biosorbent for Rapid Removal of Indigo Carmine." CLEAN - Soil, Air, Water, vol. 46, no. 6, pp. 1700186, 2018.

[13] M Mohammadi, P Lahijani and AR Mohamed, "Refractory dopant-incorporated CaO from waste eggshell as sustainable sorbent for CO_2 capture: Experimental and kinetic studies." Chemical Engineering Journal, vol. 243, pp. 455-464,2014.

[14] S Agarwal, VK Gupta, M Ghasemi and J Azimi-Amin, "Peganum harmala -L Seeds adsorbent for the rapid removal of noxious brilliant green dyes from aqueous phase." Journal of Molecular Liquids, vol. 231, pp. 296-305, 2017.

[15] HA Daraei, M Mittal, M Noorisepehr and F Daraei, "Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste." Environmental Science and Pollution Research, vol. 20, no. 7, pp. 4603-4611, 2012.

[16] S Rangabhashiyam and P Balasubramanian, "Adsorption behaviors of hazardous methylene blue and hexavalent chromium on novel materials derived from Pterospermum acerifolium shells." Journal of Molecular Liquids, vol. 254, pp. 433-445, 2018.

[17] RM Ali, HA Hamad, MM Hussein and GF Malash, "Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis." Ecological Engineering, vol. 91, pp. 317-332, 2016.

[18] S Elabbas, L Mandi, F Berrekhis, MN Pons, JP Leclerc and N Ouazzani, "Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble." Journal of Environmental Management, vol. 166, pp. 589-595, 2016.

[19] X Li, W Zheng, D Wang, Q Yang, J Cao, X Yue, T Shen and G Zeng, "Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies." Desalination, vol. 258, no. 1-3, pp. 148-153, 2010.

Supplementary

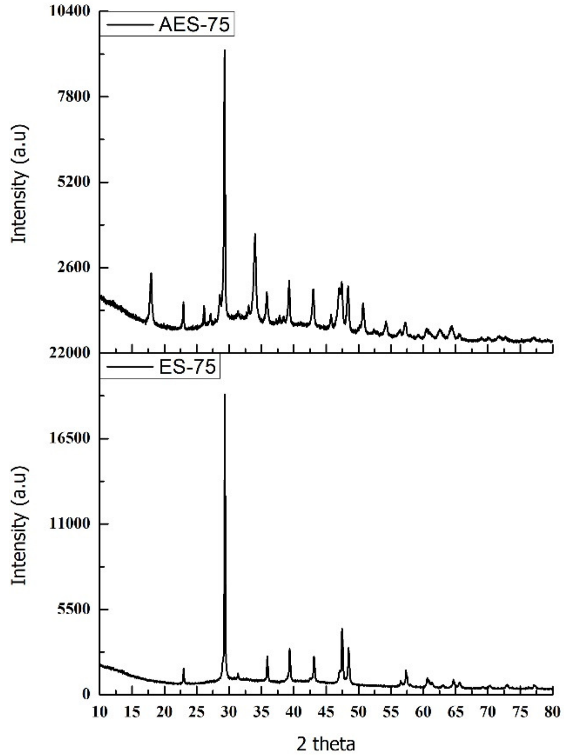


Figure S1. XRD pattern of ES-75 and AES-75

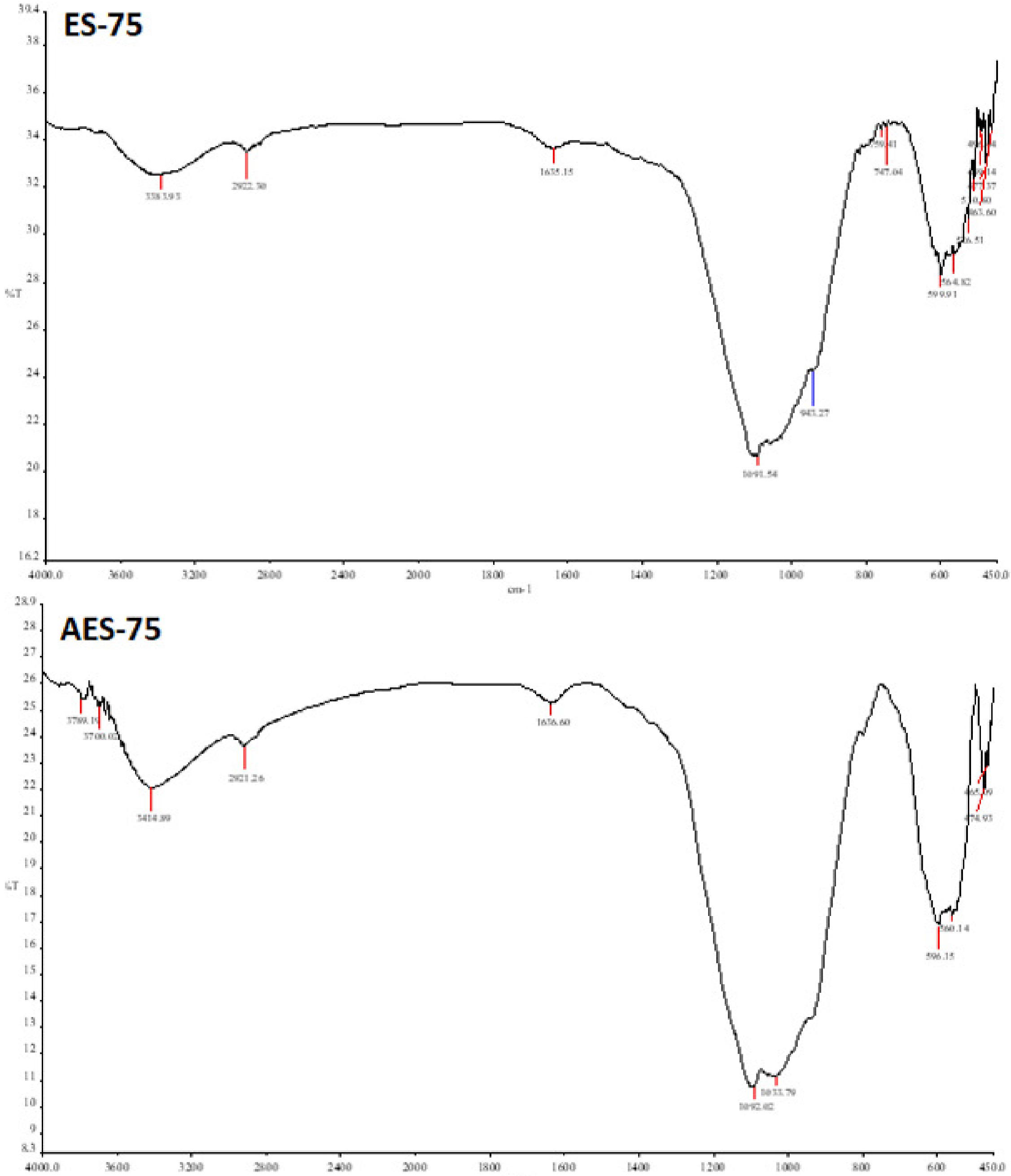


Figure S2. FTIR spectra of ES-75 and AES-75