

Evaluation of the Adsorption Kinetics and Equilibrium for the Potential Removal of Phenol Using a New Biosorbent

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Abstract

The adsorption isotherm of phenol on the eggshell (ES) and on the eggshell membrane (ESM) was performed, it revealed the eggshell biosorbents could uptake the phenol of more than 50 mg/g in aqueous medium, which was attributed to their pore properties. A comparison of kinetic models applied to the adsorption of phenol onto ES was evaluated for the first order and the second order kinetic model. The experimental data fitted very well the second order kinetic model. In the isotherm studies, the Langmuir and Freundlich isotherm models were applied. The results indicate that Langmuir equation is well solution at no pH control. Physical characteristics of ES and ESM such as presence of functional groups were verified. The Fourier transform Infra-red (FTIR) spectra proved the presence of functional groups such as hydroxyl carbonyl groups in ES and in ESM. The results indicate that ES could be fruitfully employed as a natural and Eco-friendly adsorbent material for the removal of residual phenol from effluents.

Keywords: phenol, eggshell, adsorption, waste water.

1. Introduction

The industry has often favored sites close to rivers for three reasons: to transport raw materials, to have the water which cools, to have the facilities and opportunities for discharge of industrial effluents. For decades, the rivers have inherited industrial wastewater loaded with organic pollutants and inorganic pollutants. Many studies on the rivers in the region of Meknes (Morocco) showed that natural waters are polluted by various pollutants, quoting a phenol, pollutant abundant in the region due to the activity of crushing olives and release discharge of vegetable without prior treatment in nature causing adverse effects on the aquatic ecosystem. In this respect, the environmental issues surrounding the presence of phenol in effluent are becoming to be a challenging problem, for industry. There are well documented facts that the effluents of these industries are containing suspected carcinogenic materials which are posing serious hazard to aquatic living organisms. Thus, it is necessary to reduce and eliminate these life threatening compounds from wastewater before it is discharged. The treatment of industrial wastewater is more necessary in near future due to national regulations which mandated the reduction of different compounds in the cleaned water. To obtain low phenol concentration, advanced treatment methods such as adsorption and ion exchange must be used. Adsorption is considered to be relatively superior to other techniques because of its low cost, simplicity of design, high efficiency, availability and ability to separate wide range of chemical compounds (Ru-Ling and al, 2010). It is considered that one of the major challenges faced with adsorption by activated carbon is its cost effectiveness. So, Various type of materials have been used as adsorbent, such as using chemically modified date pits activated carbons by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit (Elhachemi and al, 2009, Panumati and al, 2008), chitin and chitosane (Jian-Mei and al, 2009, Aparecida and al 2009, Dursun and al, 2005, Boukhelifi and al, 2011), a porous acrylic ester polymer and poly(methyl methacrylate) (PMMA)(Ala'a and al, 2011, Bing jun and al, 2008), clays (G.unb Busca and al, 2008, Sprynsky and al, 2009, Fuqiang and al, 2009, Yu Fei and al, 2011). The research of the recent years mainly focused on utilizing natural materials as alternatives to activated carbon. Several natural adsorbents, (Y.S.Ho and al, 1998), banana peel(Annadurai and al, 2002), orange peel (Sivaraj and al, 2001), rice husk (Arami and al, 2006), eucalyptus bark (Morais and al, 1999), bagasse pith (Chen and al, 2001) and schrimp shell (Boukhelifi and al, 2001, 2013) are some of the waste materials which have been tried for To this purpose. Among these materials we find eggshell . Hen eggshell typically consists of ceramic materials constituted by a three-layered structure, namely the cuticle on the outer surface, a calcareous layer and an inner lamellar layer (Tullett, 1987, Stadelman, 2000).

The calcareous and lamellar layers form a matrix composed of protein fibers bonded to calcium carbonate crystal. The two layers are also constructed in such a manner that there are numerous pores. This structure permits gaseous exchange throughout the shell. The cuticle is also permeable to gas transmission. The chemical composition (by weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) (Stadelman, 2000) Notably, the by-product eggshell generated from food processing and manufacturing plants is inevitably composed of calcium carbonate and eggshell membrane (ESM). The by-product eggshell represents approximately 11% of the total

weight (%60g) of egg (Stadelman, 2000). In Morocco Egg production increased by 40% between 2001 and 2010. Consumption at the national level has undergone a remarkable evolution since we spent an average of 21 eggs per year per person in 1970 to 138 in 2010 (Maâroufi, 2012). Based on the bioresource recovery and reuse, the utilization of this food processing by-product has slightly increased in recent years. Rivera (Rivera and al, 1999) reported a novel procedure to porous hydroxyapatite from eggshells. Moreover, there have been studies aiming at the calcium supplement and other nutrition sources from the albumin, membrane and matrix of the eggshell, which was processed by crushing and milling to obtain fine particles for animal use (Christmas and al, 1976). Taking into account the sustainable utilization of eggshell and its intrinsic pore structure (Rauch, 1952), the characterization of the biomaterial is very scarce in the literature.

The aim of this work was to study the removal of phenol in aqueous solution by waste eggshell (ES). In this work, reuse of ES was investigated in the viewpoint of the recycle of wastes and minimization of phenol in aqueous solution. Waste eggshell sources from house, restaurant and bakery were used as adsorbent. Toward this aim, the effect of various operating conditions on the phenol removal was investigated in batch experiments.

2. Materials and methods

2.1 Adsorption study

i. Materials

Eggshell membrane (ESM): Several studies have worked on this membrane and its use as adsorbent (Arami and al, 2006, Hernandez-Montoya and al, 2012). The eggshell membrane rinsed with deionized water repeatedly and finally dried in the oven (60°C).

Eggshell (ES) : eggshell was collected from a campus breakfast shop and immediately stored in the iced water. The hen eggshell was manually stripped from eggshell membrane after cleaning of the raw material. The eggshell rinsed with deionized water repeatedly and finally dried in the oven (60°C) for two days (Boukhelifi and al, 2000, Tsai and al, 2006). The eggshell was further ground to prepare powder particles and sieved to the required particle size of <math><0.125\text{mm}</math>. Raw eggshell (RES): was a mixture of ES and ESM.

Image 1: Summary of preparation of the adsorbent support.

2.1.2 Preparation of synthetic wastewater

Phenol solutions were prepared using distilled water $V=2\text{l}$ in $M=9,4\text{g}$ to prevent and minimize possible interference. Although in actual cases, the phenol effluent will has a different ionic strength and organic compounds and we got our solution of concentration $C = 0.05 \text{ mol / l}$.

2.1.3 Adsorption isotherm of phenol

The adsorption behaviors of eggshell particles were tentatively determined to evaluate its preferability for removal of phenol from aqueous solution. All the experiments of adsorption capacities of phenol were determined by using a batch method as described previously [Boukhelifi and al, 2011, Tsai and al, 2005].

Adsorption experiments were carried out at various concentrations of phenol solutions using optimum amount of ES (100mg) in jars containing 50ml of phenol solution. the concentration phenol was between 0,008 and 0,001mol/l, agitation speed of 200 trs/min and $20\pm 1^\circ\text{C}$ for 24h to attain the equilibrium conditions. during the adsorption process. The relatively fast equilibrium was established after 150min. The results were verified with the Langmuir and Freundlich adsorption isotherms. Adsorption isotherm was carried out at different concentration and with different particle size 600, 425, $\leq 200\mu\text{m}$.

2.1.4 Adsorption cinétique

The change on the absorbance of all samples were monitored and determined at certain time intervals (5,15, 30, 60, 90, 120,150, 180, 210,240,270 and 300 min). At the above mentioned time intervals, the samples were collected, filtered and concentration of phenol in liquid phase was determined with UV-Visible spectrophotometer.

2.1.5 UV-Vis spectrophotometer

UV-Vis spectrophotometer CECIL 2021 was employed for absorbance measurements of samples. The maximum wave length (λ_{max}) used for determination of residual concentration of phenol in supernatant solution were 185 to 380 and 380 to 800 nm respectively. Only linear range of calibration curve was used in this research.

b. Chemical characterization measurements

2.2.1. Transmission electron microscopy (TEM)

The porous texture was examined by transmission electron microscopy (TEM). The TEM analysis was carried out on the TECNAI G2/FEI. operated at a 120kV accelerating potential. Prior to the observation, the surface of the sample was coated with a thin, electric conductive gold film. Following characteristics measuring conditions : Resolution: 0.35 nm; High Voltage :120 KV, Magnification: 150 to 500 000x , microanalysis X EDS, Camera CCD, Porte object tomography $\pm 70^\circ$.

2.2.2 X-ray diffraction of ES

The spectras of X-ray diffraction were carried out by means of a powder diffractometer (model X'Pert Pro MPD panalytical) equipped with a copper anode tube. The radiation used is the $K\alpha$ line of copper ($\lambda = 1.54 \text{ \AA}$). The

spectras were recorded at room temperature. The recording conditions were as follows: tube current was 40 nA and applied voltage was 40 kV.

2.2.3 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR has been used for the examination of functional groups on the surface of eggshell before and after phenol adsorption. To obtain the observable absorption spectra, the dilution and homogenization of the dried, fine samples with KBr, were carried out with additional grinding and mixing in an agate mortar. Discs (12.7mm ID and 1mm thick) were prepared in a manual hydraulic press at about 5 tones for a pressing time of 30–60s. The spectrum was measured and recorded ($500\text{--}4000\text{cm}^{-1}$) on a spectrometer (model system 2000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0 cm^{-1} .

3 Results and discussion

3.1 Adsorption studies

3.1.1 Adsorption kinetics

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to design a fast and effective model, investigations were made on adsorption rate.

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer, several kinetics models are used to test the experimental data (Gürses, and al, 2006, Önal and al, 2007). Before the adsorption study on the first, we determine the kinetics adsorption and the time required saturation of the carrier substrate.

$$Q = \left(\frac{(C_0 - C_t)}{m} V \right) \quad (1)$$

Q: adsorption capacity of the support (mg / g). C_0 : initial concentration of phenol in the solution (mg / L) at $t = 0$: C_t : Concentration of phenol in the solution (mg / l) at time t. m : masse of adsorbent(g). V: Volume of solution (ml). P the percentage of adsorption.

$$P (\%) = 100 * (C_0 - C_t) / C_0 \quad (2)$$

Figure 1: Kinetics adsorption of phenol on eggshells (concentration of phenol $C = 0.005\text{ mol / l}$, $V = 50\text{ ml}$. ES mass $m = 0.1\text{ g}$ with grain size = $425\mu\text{m}$).

Fig. 1 shows that the adsorption increases significantly until $t = 210\text{min}$. The removal of phenol reached 52.64% and the adsorption capacity of phenol reached 123.84 mg / g . Several formulas have been used in the literature to describe the adsorption kinetics, the kinetic laws of the first and second order (Barka and al , 2008).

Kinetic order of adsorption

-The equation of the first order kinetic model is of the form (3).

$$\log_{10}(q_e - q) = \log_{10} q_e - \frac{K_1}{2.303} t \quad (3)$$

With q_e and q (mg / g), respectively, the quantities of pollutants adsorbed at equilibrium and time "t", and k_1 (min^{-1}) constant reaction kinetics of adsorption. A curve of $\log(q_e - q)$ as a function of time gives a linear shape. K_1 values were calculated from the slopes to the right.

-The equation of second order kinetic model is of the form .

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \quad (4)$$

with k_2 (mg / g.min) the second order rate constant of the reaction of adsorption. The constant k_2 may be determined from the slope of the $1 / (q_e - q)$ as a function of time.

Figure 2: Plot of the linear form of first order kinetics (5).

Figure 3: Plot of the linear form of the model from second order kinetic (6)

$$\log_{10}(q_e - q) = \log_{10} q_e - \frac{K_1}{2.303} t \quad (5) \quad (6) \quad \frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t$$

From these curves (Fig 2 and 3) it can be seen that the correlation coefficient (r^2) for the second order model is larger than that of the first order model. The second order model gives a better description of the kinetics of the adsorption reaction from the first-order model. Adsorption speed is expressed as following:

$$V = K[ES] \alpha [\text{Phenol}]^2$$

All kinetic parameters determined from these lines is collected in the table 1.

Table1: Constants of phenol adsorption kinetics for both models.

3.1.2 Adsorption isotherm

The behavior of the adsorbate vis-à-vis the adsorbent is described by isotherms (Fig.4). Adsorptions isotherms play an important role in determining the maximum capacity and identification of the type of adsorption is product.. Adsorption isotherms shows the capacity of phenol (q_e versus C_e) using ES.

Where Q_e is the amount of phenol adsorbed on ES at equilibrium, C_e the equilibrium concentration of phenol in solution.

The experimental results show that the isotherm is of type S, which corresponds to studies realised by Gilles (Giles and al.1974). This indicates growth of adsorption when the concentration of the adsorbate increases. Isotherms of this class shows at, low concentration, a concavity facing upwards. The adsorbed molecules promote subsequent adsorption of other molecules (cooperative adsorption). This is due to molecules that are attracted by Van der Waals forces, and are grouped into blocks in which they are bunched together against the other. This behavior is supported on the one hand, when the solute molecules are adsorbed vertically as is the case of molecules with a single functional group and on the other hand, when the molecules are in competition with the strong adsorption solvent (Belmouden and al, 2001) eggshells exhibit significant adsorption capacity 138.84 mg / g at a concentration of 0.0061 mol / l.

To optimize the design of an adsorption system for the adsorption of phenol, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Langmuir and Freundlich were tested in this work.

Langmuir isotherm

In the Langmuir theory (7),the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. This equation can be written as follows (Hiemenz, 1986, Stumm and al , 1981) :

$$\frac{Q}{Q_m} = \frac{KC_e}{1 + KC_e} \quad (7)$$

Where Q is the amount of phenol adsorbed on ES at equilibrium, C_e the equilibrium concentration of phenol solution, K the equilibrium constant and Q_m is the maximum adsorption capacity. The linear form (8)of Langmuir equation is:

$$\frac{1}{Q} = \frac{1}{Q_m} + \frac{1}{K \cdot Q_m} * \frac{1}{C_e} \quad (8)$$

Adsorption of phenol on eggshells from equation linearization can deduce the parameters of Langmuir, we find $Q_m = 45.4545$, $K = 1, 1322 \cdot 10^{-3}$.

The essential characteristic of the Langmuir isotherm (Fig. 5) can be expressed by the dimensionless constant called equilibrium parameter, R_L ,

Where b is the Langmuir constant and C_0 is the initial dye concentration (mmol/L), R_L values indicate the type of isotherm to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or un favorable ($R_L > 1$)(Wan Ngah and al, 2005). The R_L (9) values for the adsorption of phenol on ES have been shown in table 2.

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Freundlich isotherm (Fig. 6) can be expressed by Stumm and al, 1981).

Where K_F is adsorption capacity at unit concentration and $1/n$ is adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n=0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$) (Stumm and al, 1981). Equation (10) can be rearranged to a linear form.

$$Q_e = K_f C_e^{1/n} \quad (10)$$

The $1/n$ values for the Freundlich adsorption isotherm have been shown in Table 2.

The value of $1/n$ gives an indication of the validity of the adsorption of the adsorbate-adsorbent system. A value of $1/n$ between 0 and 1 indicates a favorable adsorption (Tsai and al, 2005).

The values of R^2 computed by linear regression for the all investigated types of isotherms are presented in Table 2. The Table 2 indicate that the langmuir isotherm is most appropriate for adsorption of phenol on ES.

3.2 Characterization of the eggshell : Mechanism of adsorption

3.2.1 Transmission electron microscopy (TEM) of ES

MET-EDX has been an essential tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. From Fig. 9, it is clear that, ES has considerable numbers of pores where, there is a good possibility for phenol to be trapped and adsorbed into these pores. The MET-EDX pictures of ES samples show very distinguished dark spots which can be taken as a sign for effective adsorption of phenol molecules in the cavities and pores of this adsorbent.

3.2.2 X ray-diffraction:

X-ray diffraction results of the ES after and before adsorption are reported in Fig.10. Main reflections corresponding to calcium carbonate crystalline phases (CaCO_3). It seems clear from the results XRD analysis of the ES that the reflections of CaCO_3 decrease after adsorption. Phase of calcium carbonate has not changed after adsorption proving that the phenol does not react with the surface but there is a physical interaction between the adsorbent and phenol.

3.2.3 Fourier transform infrared spectroscopy (FTIR) analysis of ES

The observation described above was also demonstrated by the FTIR spectra, shown in Fig. 11. This figure shows before adsorption, the most significant peak of intensity of eggshell particle at 1417cm^{-1} , strongly associated with the presence of carbonate minerals within the eggshell matrix [43]. There are also two observable peaks at about 712cm^{-1} and 875cm^{-1} , respectively, which should be associated with the in-plane deformation and out-plane deformation modes, respectively, in the presence of calcium carbonate (Busca, 2000).

The phenol is characterized by two bands, one is located at $1400\text{-}1320\text{cm}^{-1}$ characterizing the deformation of O-H and the other to the elongation $1300\text{-}1150\text{cm}^{-1}$ characterizing C-O, in solution in an apolar solvent, a fine peak is observed at 3610cm^{-1} . It is the stretching vibration of the O-H free. For the pure compound, The results shows that there is a broad band $3200\text{cm}^{-1} < \nu < 3400\text{cm}^{-1}$. These links O-H associated by intermolecular hydrogen bonding. we note that in our case, the maximum adsorption is achieved for a wave number which is 1408cm^{-1} , this value coincides with the breaking of the OH bond. This is confirmed by the second band at 880cm^{-1} . The OH bond of phenol was modified by the medium.

3.4 Interpretation and retention mechanism

Phenol is a hundred million times more acidic than cyclohexanol. Therefore, it is deprotonated quantitatively by a basic solution to give a phenolate solution. From experience the presence of eggshells in water makes the basic medium $\text{pH} = 8$. In contact with a solution of phenol, phenol deprotonates the adsorbate leading to an interaction between calcium and phenol (mechanism 1). The adsorbent cannot be deprotonated attracted by the surface of eggshells by a hydrogen bond between oxygen and hydrogen of phenol (mechanism 2). (Image 2)

The negative charge dispersed in the cycle is better supported by the structure and the resulting stabilization is responsible for the loss of basicity. therefore, phenols are much weaker bases $\text{pK}_a (\text{PhO}/\text{PhOH}) = 7$. This can be interpreted by a protonation basicity of oxygen much more difficult because of the relocation of the doublet.

4. Conclusion

The present study attempted to show that the hen eggshell and eggshell membrane particles were an effective adsorbents for the removal of phenol from aqueous solutions. The most important factors to design and run an industrial adsorption plant are the knowledge of adsorption kinetics and isotherms. It was found that, adsorption of phenol onto ESM obeys Langmuir isotherm. For phenol, the adsorption capacity increased with the decrease in particle size. The kinetics studies of phenol on ESM and ES were performed based on second order rate mechanisms. By the observations in the FTIR spectra, eggshell particle is strongly associated with the presence of carbonate minerals within the eggshell matrix.

The mechanism of adsorption was explained by interaction between negative site of phenol and carbonate surface. The pH of the phenol solution is a very important parameter since it affects the phenol adsorption capacity of ES. At alkaline pH a significantly high electrostatic exists between the negatively charged surface of the adsorbent and eggshell.

This work shows that waste eggshells can be evaluated using a simple procedure of preparation for the treatment of wastewater polluted by phenol.

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Table1. Constants of phenol adsorption kinetics for both models.

Adsorbant	k_1	r^2	k_2	r^2
ES	0,004606	0,765	0,006	0,9664

Table 2. Main parameters characterizing the two models of adsorption of phenol on ES.

Modèles	Q_m (mg/g)	k (L.mg-1)	kf (mg/g)	n	R (correlation coefficient)
LANGMUIR	50	1,174.10-3	-	-	0,992
FREUNDLICH	-	-	1,129.10-4	0,466	0,972

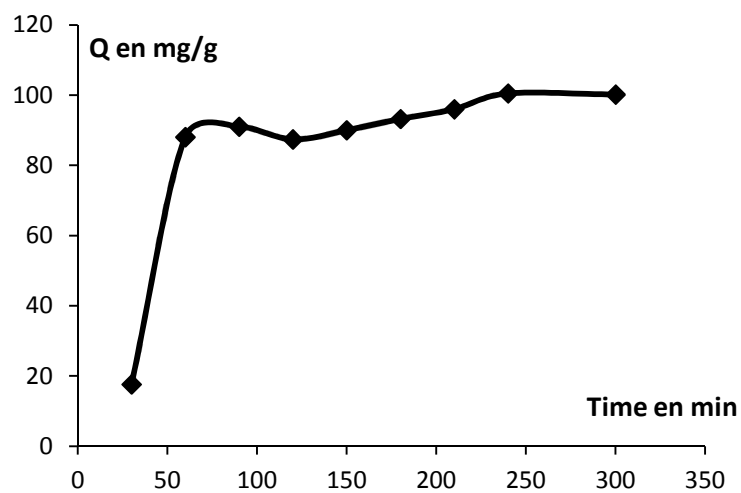


Figure 1: Kinetics adsorption of phenol on eggshells (concentration of phenol $C = 0.005$ mol / l, $V = 50$ ml .ES mass $m = 0.1$ g with grain size = $425\mu\text{m}$).

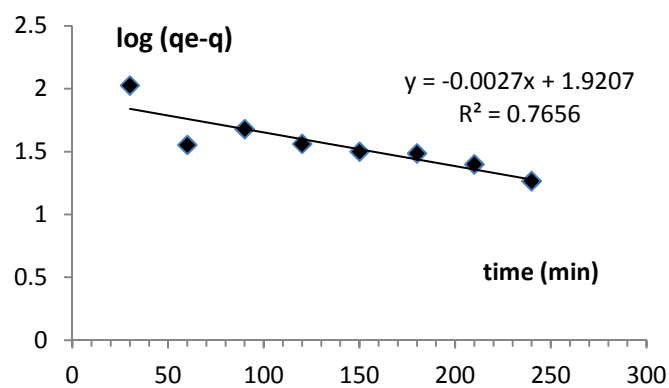


Figure 2: Plot of the linear form from first order kinetics.

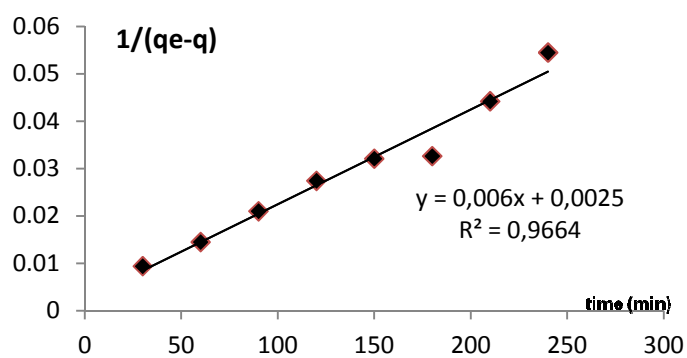


Figure 3: Plot of the linear form of the model second order kinetic (6)

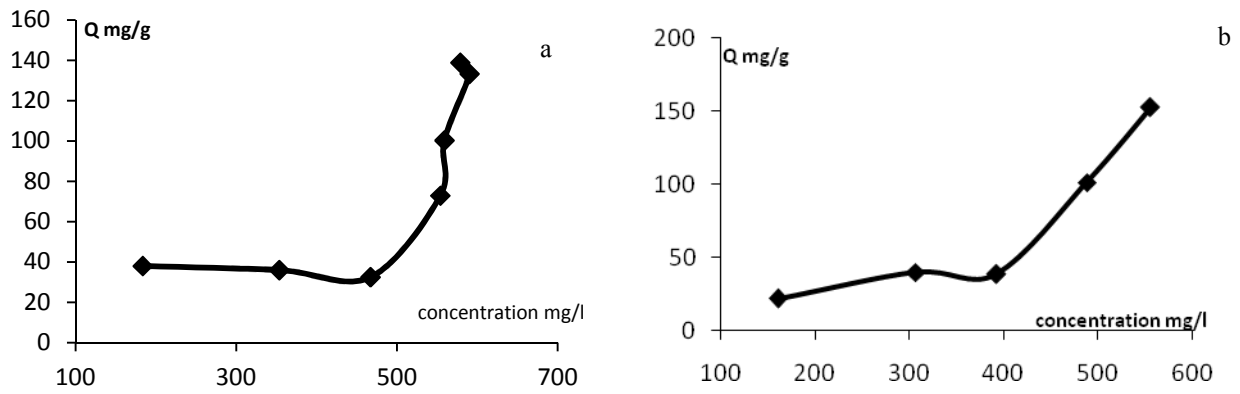


Figure 4: a) Adsorption isotherm of phenol on ES, V=50ml m=0,1g t=210 min

b) Adsorption isotherm of phenol on ESM V=50ml, m=0,1g, t=210 min

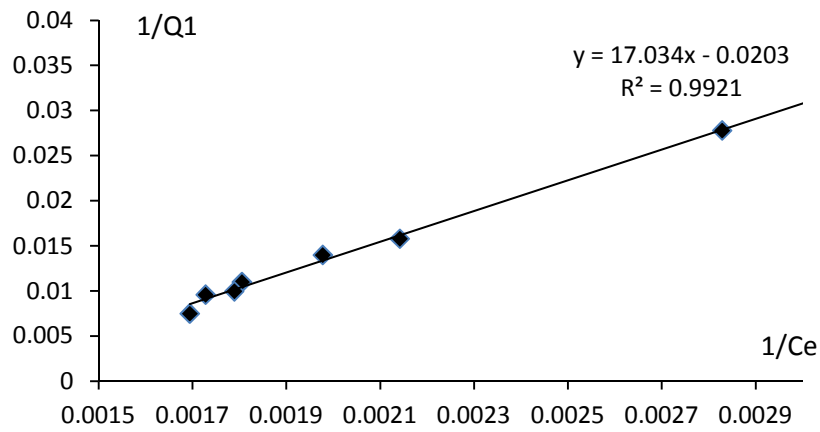


Figure 5: Linear model of Langmuir for adsorption of phenol on ES

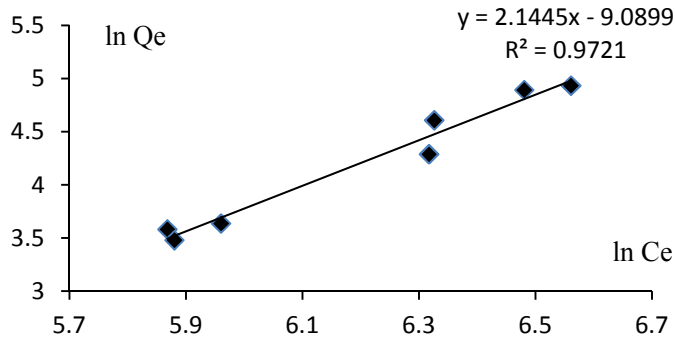


Figure 6: Linear model of Langmuir of adsorption of phenol on ES

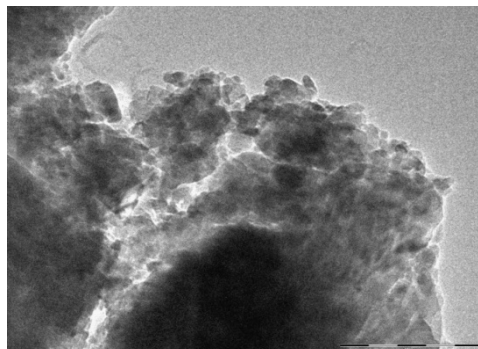


Figure 7: TEM images of egg-shell nanostructures (200 nm).

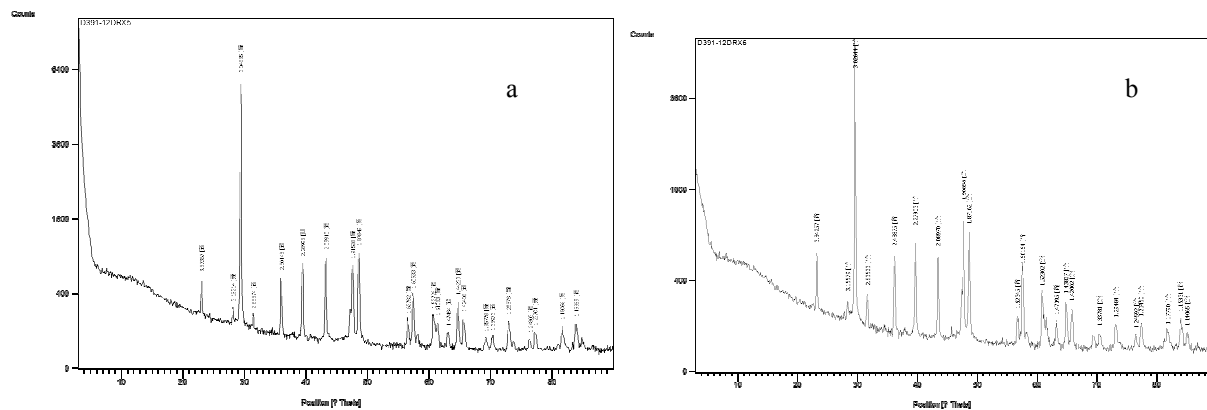


Figure 8: a) X-ray diffraction of ES before adsorption b) X-ray diffraction of ES after adsorption

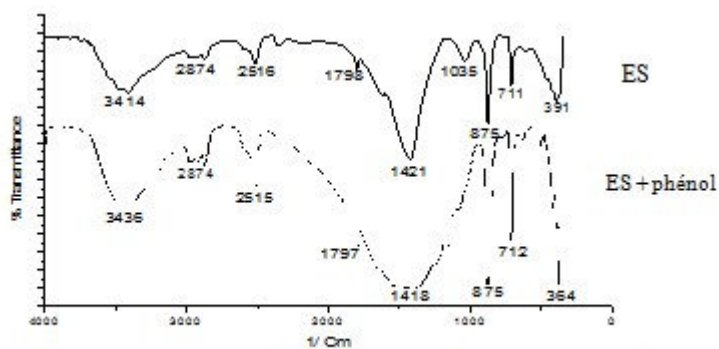


Figure 9: The FTIR spectra of ES before and after adsorption of phenol

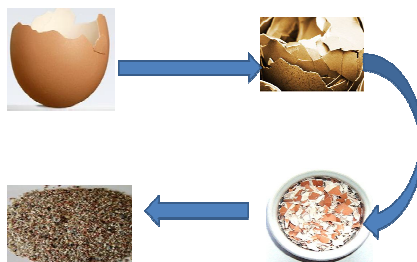


Image 1: Summary of preparation of the adsorbent support.

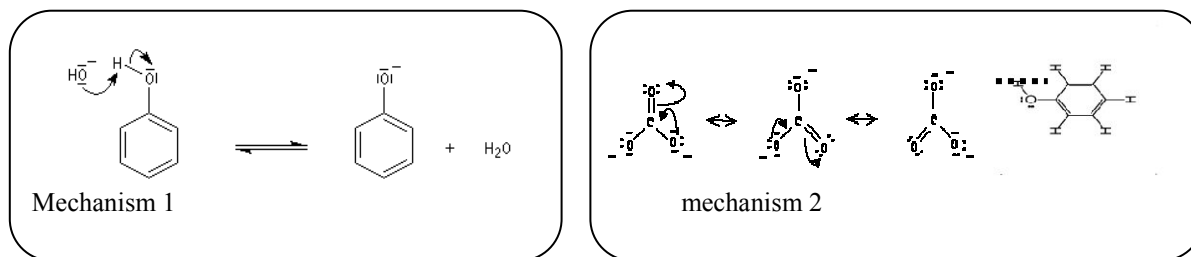


Image 2: mechanism of phenol retention

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