Kinetics and equilibrium of phosphate adsorption onto chemically activated carbon prepared from date stones

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Abstract

The present study was performed to investigate the preparation of activated carbon from date stones for its possible use in removing phosphates ions from aqueous solution. Date stones activated carbon (DSAC) was prepared by chemical activation using sulfuric acid as activating agent. The prepared activated carbon was characterized by scanning electron microscopy and Fourrier transformation technique. Batch adsorption experiment was the performed to evaluate phosphate ions removal by date stones activated carbon. The equilibrium contact time for phosphate ions removal by date stones activated carbon was attained after 240 min. Kinetic modeling of phosphate adsorption was investigated using the Pseudo first-order and Pseudo second-order rate equations. The experimental data of phosphate adsorption by DSAC were best described by the Pseudo second-order kinetics model. The equilibrium modeling study revealed that the Freudlich isotherm model gave a better fit to the experimental data of phosphate removal by DSAC than the Langmuir and Temkin isotherms. The present study highlights the use of a locally available waste (date stones) as a precursor material for the preparation of a cost effective adsorbent.

Keywords: Date Stone; Chemical Activation; Phosphate Ions; Adsorption; Kinetics; Equilibrium

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1. Introduction

The removal of phosphates from water environment is one of the most important scientific research concerns. Phosphates are released into the water environment as wastes of several industrial and agricultural applications. These applications of phosphates include fertilizers detergents, water softening, food and drinks, metallurgy, etc. (Karageorgiou et al., 2007). The presence of phosphates in water stimulates thegrowth of aquatic micro and macro organisms leading to eutrophication and impairment of water bodies(Ragheb, 2013). In many countries the concentration of phosphorus discharged into water is limited to 0.5-1 mg/l (Benyoucef and Amrani 2012; Ragheb, 2013).

The removal of phosphates from water was usually carried out by chemical precipitation using calcium chloride or lime (Namasivayam et al., 2005). However, the broad application of this chemical method may be limited because of the cost of metal salts used as well as the production of metal phosphate sludge as a waste (Karageorgiou et al., 2007).

One of the promising removal methods that could be employed for pollutants removal is adsorption. Different types of adsorbents are used in adsorption process of which activated carbon could be the most efficient. The adsorption properties of activated carbon strongly depends on the activation procedure, which are physical or chemical activation as well as the nature of the precursor materials used (Gerçel et al., 2007; Li et al., 2010). Nowadays, there is an increasing concern about the finding of cheaper precursors which are generally industrial and agricultural wastes (Theydan and Ahmed, 2012).

The use of date stones for the preparation of activated carbon has been investigated by several authors for the removal of different pollutants including organics and inorganics (Theydan and Ahmed, 2012; Bouhamed et al., 2012). Egypt has the largest production of dates considered as 16.9% of worldwide production (Chao and Krueger, 2007). Thus the reutilization of wastes from palm oil factories considered as environmental contamination source could be beneficial (Theydan and Ahmed, 2012). In the present work, we investigate the preparation of activated carbon from date stones for the removal of phosphates from wastewater as an economic and environmental friendly way of wastewater treatment.

2. Materials and methods

All chemicals used were of analytical grade purchased from Sigma Co.

2.1. Preparation of date stones activated carbon (DSAC)

Date stones were washed and then oven dried at 110°C for 4 hrs. The dried stones were then heated in a muffle furnace at a rate of 10°C/min from room temperature to 600 $^{\circ}$C and maintained at this temperature for 2 hrs. The chemical activation was performed using H_2SO_4 as activating agent following the procedure described by (Kilpimaa et al., 2014). In brief, dried ash was treated with 0.1 M H_2SO_4 at a ratio of (1:10), then

dried at 110◦C overnight and further activated at 500◦C. The resulting activated carbon was then washed, dried at 110◦C overnight, crushed and sieved and designated as date stones activated carbon (DSAC).

2.2. Characterization of DSAC

The surface characteristics of DSAC were examined by Scanning Electron Microscopic technique using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n).

The functional groups of the prepared activated carbon (DSAC) were determined using Fourier Transformation infrared technique by a Perkin-Elmer FT-IR 1650 spectrophotometer with working range (200-4000 cm^{-1}).

2.3. Batch adsorption experiments

Batch experiments were performed at different contact time (30, 60, 90, 120, 150, 180, 240 and 360 min.) and at different phosphate ions concentration (5, 15, 25, 50 mg/l). In each batch experiment, solution pH was kept at 6 and a 25 ml phosphate solution was mixed with a 0.05g DSAC in a conical flask. The flasks were then agitated placed in a shaking water bath at 150 rpm at room temperature and mechanically shaken until equilibrium was reached. The mixture was then filtered and the remaining phosphate concentration was determined using a SpectroD 250 UV/Vis spectrophotometer, Analytik Jena.

The amount of phosphate adsorbed at equilibrium (adsorption capacity), q_e (mg/g), was calculated by the following equation:

$$q_e = \left[\frac{C_i - C_e}{w}\right] * V$$

Whereas phosphate removal percentage (R %) was calculated by the following equation:

$$R\% = \left[\frac{C_i - C_e}{C_i}\right] * 100$$

Where C_i and C_e represent phosphate ions concentration at the initial time and at equilibrium (mg/l), respectively; while V represents the volume of the solution (l) and W is the mass of adsorbent used (g).

2.4. Kinetics study

In order to investigate the kinetics of phosphate adsorption onto DSAC, the pseudo-first order and pseudo-second order kinetics models were tested to fit the experimental data.

The linear form of pseudo first order equation (Lagergren, 1898) is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (eq.1)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of phosphate ions adsorbed at equilibrium and at time (t), respectively, k_1 (min^{-1}) is the pseudo first order rate constant. q_e and k_1 are determined from the intercept and slope, respectively of the plot of ln(q_e–q_t) versus (t).

The pseudo second order model (Ho and McKay, 1998) equation is presented as:

$$t/q_t = 1/ k_2 q_e^2 + t/q_e \qquad \text{(eq. 2)}$$

where k_2 (gmg^{-1}min^{-1}) is the rate constant of the second order equation. q_e and k_2 can be determined from slope and intercept, respectively of the plot of (t/q_t) versus (t).

The intra-particle diffusion model was also applied to the data of the present study. The model's equation as given by Weber and Morris (1963), can be expressed as follows:

$$q_t = K_t^{0.5} + C_b \qquad \text{(eq.3)}$$

where q_t is the adsorbed quantity of pentachlorophenol, K is the intra-particle diffusion parameter, and C_b is the thickness of the boundary layer.

2.5. Equilibrium study

The equilibrium modeling for phosphate ions adsorption onto DSAC was investigated by applying three models namely: Langmuir, Freundlich and Temkin.

The linear form of Langmuir isotherm equation (Langmuir, 1918) is given as: $q_e = q_{max} b C_e / (1 + bC_e)$, the linear form of Freundlich equation (Freundlich, 1906) is given as: $Log q_e = log K_f + 1/n \ log C_e$, the Temkin isotherm equation (Temkin and Pyzhev, 1940) is given as: $q_e = a_t + b_t ln C_e$, where: q_e and C_e represents the adsorbent capacity at equilibrium (mg/g) and the concentration of phosphate at equilibrium (mg/l). In the Langmuir equation, q_{max} is considered the maximum sorption capacity related to the total surface coverage and b is related to sorption energy. From the Freundlich model, K_F represents the sorption capacity and $1/n$ is related to the energy distribution of the sorption sites. The Temkin model constants a_t and b_t are related to the maximum binding energy and heat of adsorption.

3. Results and discussion

The effect of contact time on phosphate removal by DSAC was studied at room temperature using a phosphate solution of 25 mg/l concentration in the time range from 30 to 360 min. The effect of contact time on phosphate removal by DSAC is shown in Figure 1. It is generally agreed that the wastewater treatment cost depends significantly on shaking time because it is consuming energy; thus it is important to find the optimal contact time needed to achieve maximum removal (Simsek et al., 2013).

From (Figure 1) it can be seen that the removal of phosphate ions started to increase by increasing contact time before finally reaching its equilibrium after 240 min. Therefore in the present work, the optimum contact time was kept at 240min for further experiments.
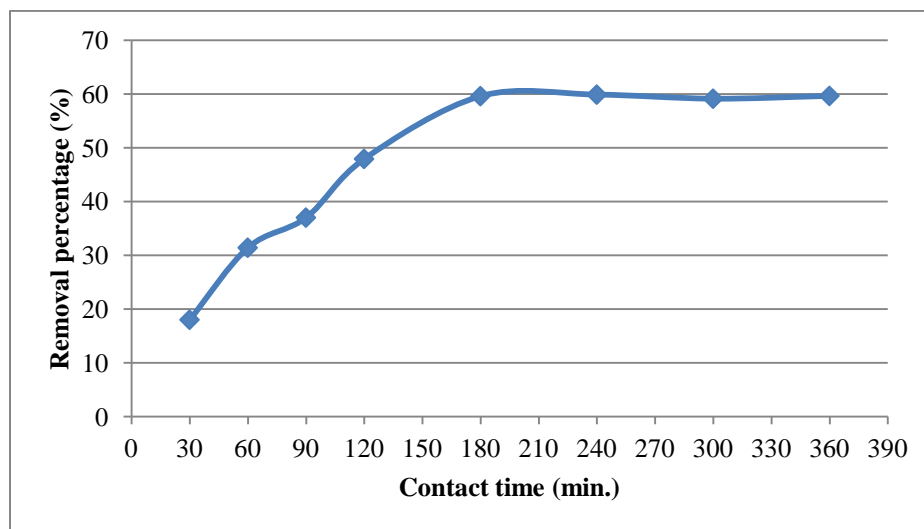
Figure 1. Effect of contact time on phosphate removal onto DSAC (initial ions concentration= 25mg/l; pH=6; adsorbent weight 0.05g/ 25 ml)

Adsorption kinetics is an important factor to assess the adsorption efficiency(Dural et al., 2011). In the present study, the kinetic modeling of phosphate adsorption by DSAC was investigated using the Pseudo first-order and Pseudo second-order rate equations. Figures 2 and 3 show the linear plots of ln (qe-qt) vs (t), and of t/qtvs (t) representing the Pseudo first-order and Pseudo second-order, respectively. The parameters of the pseudo-first order and the pseudo-second order kinetics models, calculated from the linear plots, together with the corresponding correlation coefficients (R^2) are summarized in Table 1.
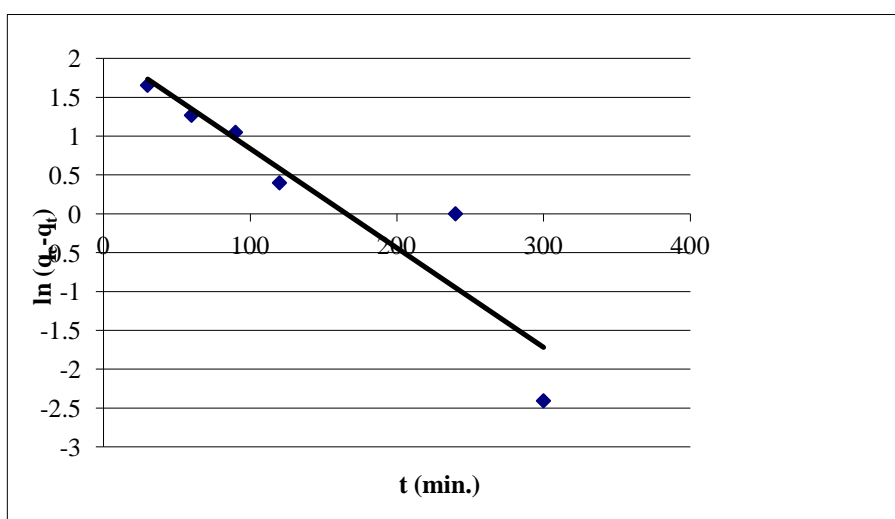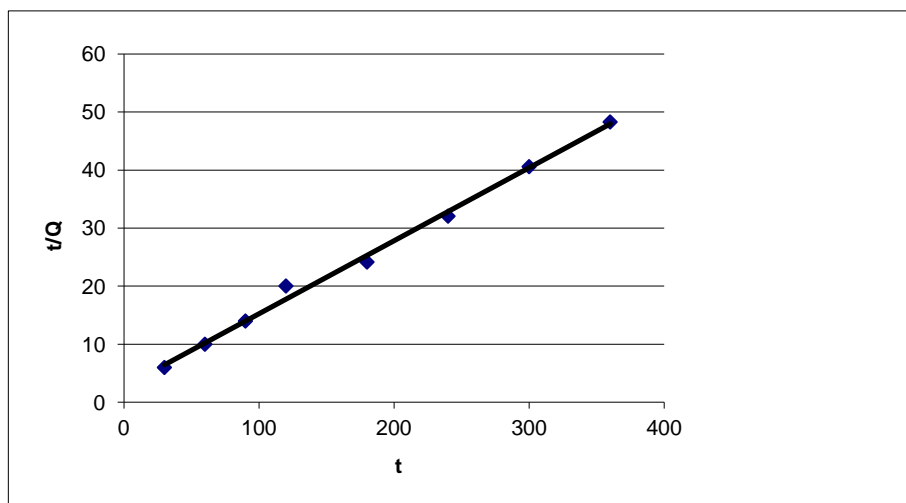

Figure 2. Pseudo first-order kinetics plot

Figure 3. Pseudo second-order kinetics plot

As shown in (Table 1), it is noticeable that the correlation coefficients ($R^2 > 0.99$) for the pseudo-second order kinetic model is higher than that of the pseudo-first order kinetic model. Also the valueofq_e,calculated from the pseudo-second order kinetic model is closer to the experimental qevalue (q_e,exp) compared to the q_e, calculated from the pseudo-first order kinetic model. These results clearly indicate that the experimental data of phosphate adsorption by DSAC are best described by the Pseudo second-order kinetics model.

Table. 1. kinetic models' constants for phosphate adsorption by DSAC.

First-order kinetic model				Pseudo-second-order model				Intra-particle diffusion model			$q_{e, Exp}$ (mg/g)
$K_{1,ad}$ min^{-1}	$q_{calc.}$ (mg/g)	R^2	Δq	$K_{2,ad}$ (g/mg.min)	$q_{calc.}$ (mg/g)	R^2	Δq	K (mg/g min$^{-0.5}$)	C_b (mg/g)	R^2	
0.012	8.31	0.886	0.83	5.77×10^{-3}	8.00	0.995	0.52	0.1622	0.578	0.980	7.48

The adsorption of phosphate ions onto DSAC was further assessed from a mechanism view by applying the intra-particle diffusion model to the obtained experimental data. Fig. 4illustrates the plot of intra-particle diffusion model showing only one straight line that is not passing by the origin. This result suggest that the adsorption kinetics may be controlled by film diffusion and intra-particle diffusion simultaneously(Khalil et al., 2013). Table 1 shows the values of the intra-particle diffusion rate constant (K) and the thickness of the boundary layer (C_b) as obtained from the plot of qt versus $\sqrt{t}$.
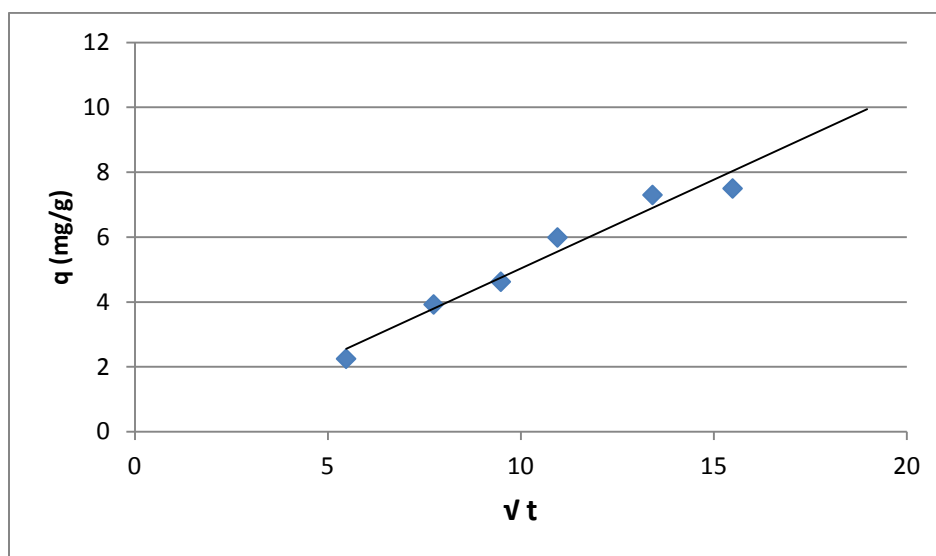
Figure 4. Plot of intra-particle diffusion model for the adsorption of phosphate ions onto DSAC.

Adsorption equilibrium isothermal models are usually used to elucidate the surface properties and affinity of adsorbent for different adsorbents. In the present work, three famous isothermal models were tested to fit the equilibrium data namely: Langmuir, Freundlich and Temkin. The isotherm parameters and correlation coefficients are tabulated in Table 2.

The Langmuir isotherm model assumes monolayer sorption onto a surface with a finite number of identical sites (Pahlavanzadeh et al., 2010). The Langmuir parameters are obtained from the plot of (C_e) versus (C_e/q) as given in Figure 5.

The Freundlich isotherm model describes the adsorption on heterogeneous surface and is not restricted to the formation of monolayer (Bulgariu and Bulgariu, 2012). The Freundlich parameters are calculated from the plot of log q against log C shown in Figure 6.

The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich model (Cayllahua and Torem, 2010). Figure 7 gives the plot of q against lnCe from which the Temkin constants are obtained.

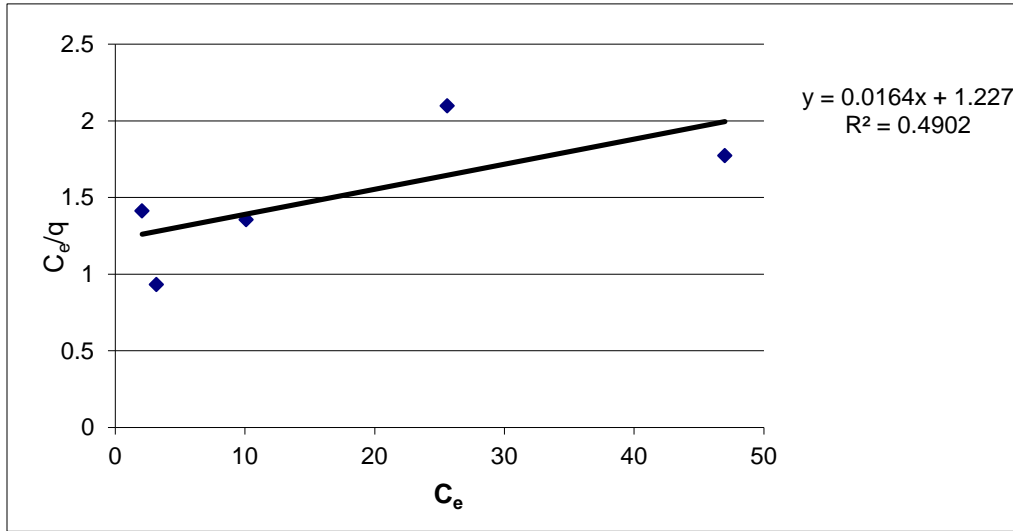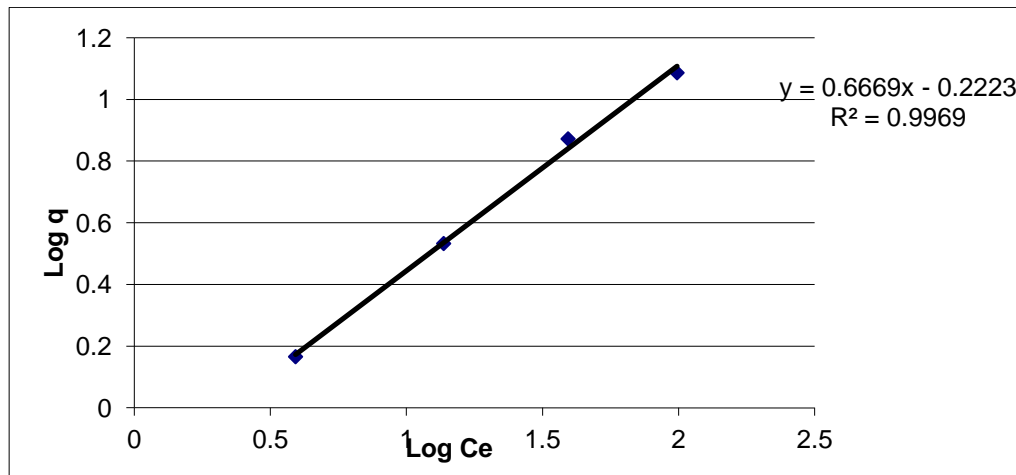**Figure 5.** Langmuir isotherm plot

Figure 6. Freundlichisotherm plot (n=1.5, K_F = 0.65)

The results of the equilibrium modeling study revealed that the Freudlich isotherm model gave a better fit to the experimental data of phosphate removal by DSAC than the Langmuir and Temkin isotherms as shown by its higher R^2 value(R^2>0.99). The better fitting of Freundlich model suggests that DSACisenergetically heterogeneous and porous since the Freundlich equation is more suitable for highly heterogeneous surface(Chaudhry et al., 2017).According to Benyoucef and Amrani (2011), the Freundlich constant (n) refers to the interaction between exchange sites in the adsorbent and phosphate ions and when n is higher than unitythis indicates favorable adsorption. In our present study (n) value obtained from the model was found

to be 1.5 which is indicative of a constant partitioning of the sorption mechanisms, where sorbate penetrated the sorbent and therefore showed good adsorption (Javaid et al., 2011).
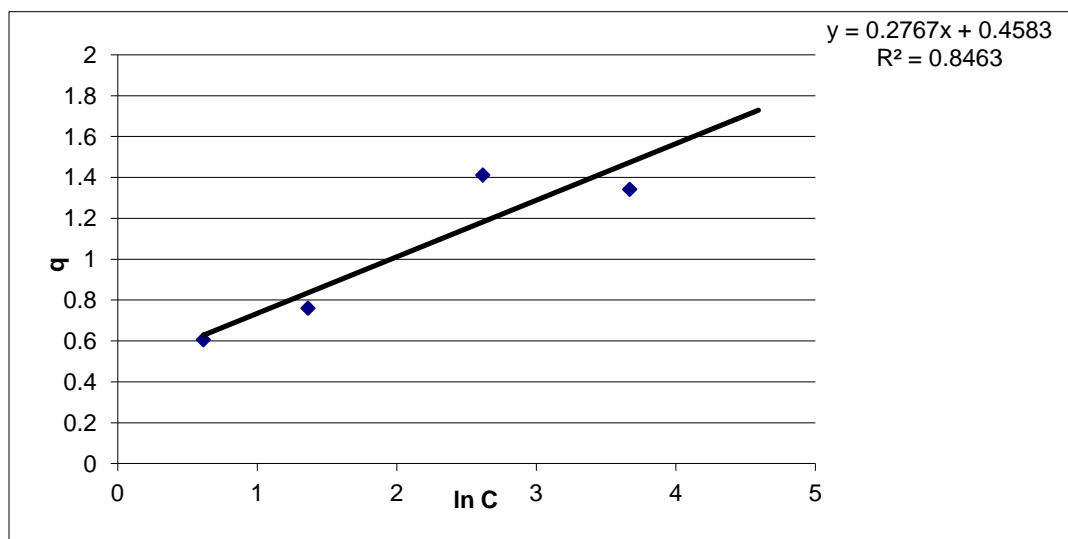

Figure 7. Temkinisotherm plot

Figure 8 gives the SEM micrograph of DSAC showing its surface features of at a magnification of 1000 X. The prepared carbon has a highly porous texture with a large, accessible surface area that favors sorption (physical sorption)(Tang et al., 2013).
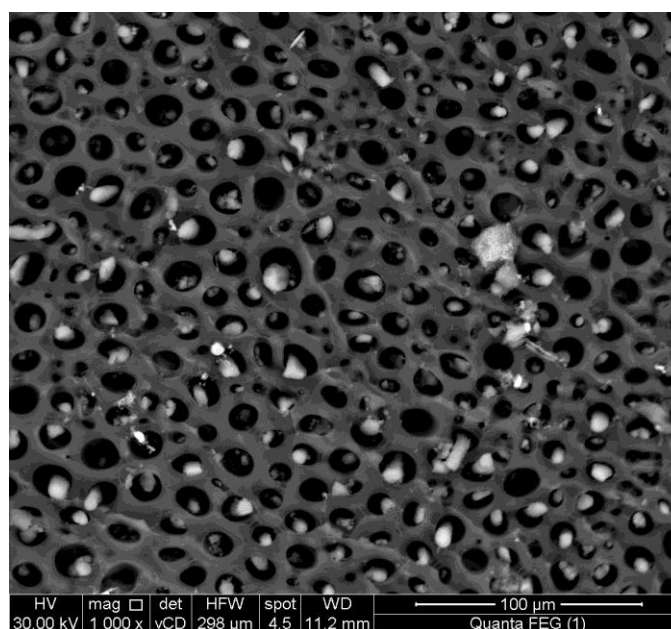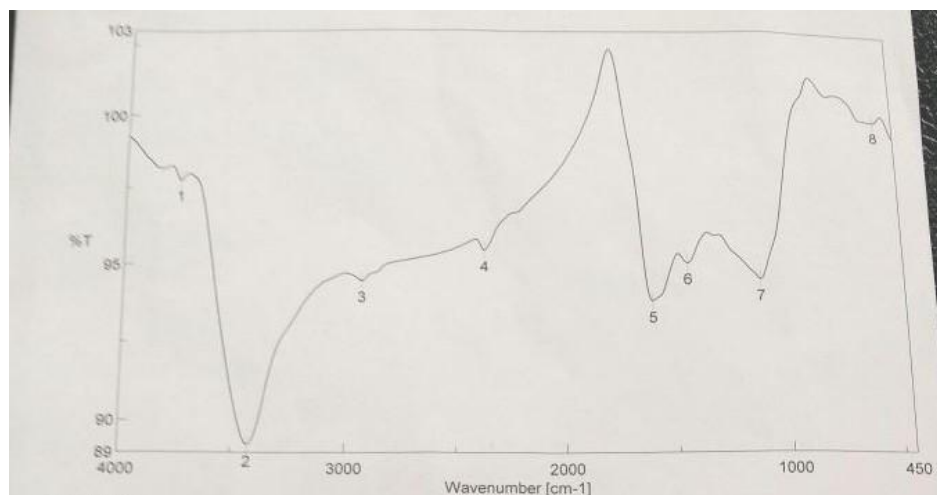

Figure 8. SEM micrograph of DSAC (1000X)

Figure 9. FTIR spectrum of DSAC

The FTIR spectrum of DSAC is displayed in Figure9, the FTIR spectrum obtained for the prepared activated carbon displayed several major bands. The first band observed in DSAC spectrum 3427.85 cm^{-1} was assigned to the stretching of H-bonded of OH groups (Zheng et al., 2010). Another band at 2923.56 cm^{-1}can be assigned to the C–H group, whereas that one observed at 2366.23 cm^{-1}signified C-H stretching position (Auta and Hameed, 2011). The peak around 1605.45cm^{-1}can be ascribed C=C aromatic ring stretching vibration (Momčilović et al., 2011), while that at 1445.39 cm^{-1}provides information about the presence of C=O and N-H groups (Ghaedi et al., 2013). The bands at 1116.58 – 541.899cm^{-1} indicate the existence of some inorganic sulfates and silica Si O Si asymmetric stretch (Auta and Hameed, 2011).

4. Conclusion

The removal of phosphate ions from water was successfully achieved by using activated carbon prepared from date stones. The adsorbent efficiency was attributed to its porous structure and presence of several functional groups on its surface. The adsorption process was best described by the Freundlich equilibrium model indicating physical adsorption and the results revealed favorable adsorption. The present study highlights the use of a locally available waste (date stones) as a precursor material for the preparation of a cost effective adsorbent. Further studies could be done to investigate other adsorption parameters and to investigate the application on real wastewater system.

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