

Removal Capacity of Cadmium in Aqueous Solution via Activated Carbon of Coke Breeze and Date Seeds

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Abstract—This paper focused on preparation activated carbon from industrial and agricultural wastes, and physico-chemical properties were carried out to show adsorption process. The adsorption of cadmium from liquid solutions onto activated carbon of coke breeze and date seeds has been investigated in the current study. The process was studied in a batch system with respect to the contact time, temperature, adsorbent weight, initial cadmium concentrations, and PH does. The results also indicated that process of cadmium uptake by activated carbon of coke breeze or activated carbon of date was physical adsorption process. The equilibrium data for date seeds indicated that it fitted both Freundlich and Langmuir models. However, adsorption onto carbon of coke breeze or activated carbon of date seeds fitted Langmuir models better based upon the higher value of regression R^2 obtained, and adsorption process for ACs used followed pseudo second order reaction. These adsorbents were found to be both effective and economically viable.

Keywords— Adsorption, activated carbon of coke breeze, and cadmium removal.

I. INTRODUCTION

Wastewater discharged from a number of industrial activities such as mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides production play a major role in the introduction of these toxic metal ions into the aquatic streams (Sud et al., 2008, Wang and Chen, 2009). Because of their persistence in the environment and their recalcitrant nature, these metals can accumulate in living tissues and become concentrated throughout the food chain (Martín et. al., 2005). Subsequently, their removal and remediation from aqueous streams has become a priority for water resource conservation and safe use.

Heavy metal ions of more concern are arsenic, cadmium, chromium, lead and mercury as they pose a serious threat to living organisms (Khan et al., 2008). These heavy metals may enter the human body through food, air and water and small concentration of these elements may cause acute or chronic toxic effects (Amin et al., 2013). In addition, heavy metals affect growth, yield and quality of the crops (Singh and Agrawal 2010). Cadmium is a metal of most toxicological concern because of its bioaccumulation and non-biodegradability even at low concentrations (Waalkes 2000). Cadmium is widely used in batteries (nickel-cadmium

batteries), pigments, alloys, phosphate fertilizers and metal plating (John and Santhi, 1994-Lambert et al., 2007). Galvanized pipes, discharge from metal refineries, ash of combustion of fossil fuels, runoff from waste batteries and paints are the important sources of exposure of cadmium in water.

Cadmium (Cd) is a chemical element and atomic number 48. This soft, bluish-white metal, it has a lower melting point than the transition metals. The average concentration of cadmium in Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered as an impurity in zinc carbonate.

Cadmium occurs as a minor component in most zinc ores and is a byproduct of zinc production. Cadmium was used for a long time as a corrosion-resistant plating on steel, and cadmium compounds are used as red, orange and yellow pigments, to color glass, and to stabilize plastic. Cadmium use is generally decreasing because it is toxic and nickel-cadmium batteries have been replaced with nickel-metal hydride and lithium-ion batteries. One of its few new uses is cadmium telluride solar panels.

The rapid growth of economy has worsened the environmental pollution, also accompanied with the call for the construction of ecologically civilized society. Activated carbon (AC) is an efficient material for the control of environment pollution, which is extensively applied in liquid-phase and gas-phase pollution. AC preparation by phosphoric acid from agriculture and forestry wastes, such as cotton stalks (Girgis, and Ishak, 1999 - Nahil, and Williams, 2012), Arundo donax cane (Vernersson et al., 2002), tobacco stems (Li et al., 2008), sugar cane bagasse (Liou, 2010), sunflower seed hull (Liou, 2010), globe artichoke leaves (Benadjemia et al., 2011), Cyperus alternifolius (Sun, et al., 2012), Acacia mangium wood (Danish et al., 2013), date stems (H. Hadoun et al., 2013), date (Phoenix dactylifera L.) stone (M. Danish, et al., 2014), reedy grass leaves (Xu et al., 2014), cocoa shells (Pereira et al., 2014), siriguela seeds (Pereira et al., 2014), etc.

The date seed is a waste product of date fruit which is largely grown in the Middle East Asia, North African and North American desert region. There are large numbers of

palm trees in Oman and thus the amount of dates are largely available which is economically viable material for the production of activated carbon from DS. It is on an average about 10% of the total weight of a date fruit. The chemical composition of date stone consists of hemicelluloses (23%), lignin (15%), cellulose (57%) and ash (5%) (Haimour and Emeish, 2006). Carbon black or activated carbons are currently the most widely used materials for water treatment because of their high specific surface area and moderate cost (Gilbert et al., 2012). The removal of a chemical from solution by activated carbon is a mass-transfer process in which the chemical is bonded to the solid which is called adsorption. The chemical (the adsorbate) penetrates into the pores of the solid (the adsorbent), but not into the lattice itself. Recently DS have received considerable attention as a ligninorigin material for preparing low-cost activated carbon. There are two types of activation which are; physical activation and chemical activation. Physical activation is done by contacting the char with an oxidizing gas, such as carbon dioxide, steam, air or their mixtures, in the temperature range between 600 and 900 °C, which results in the formation of a well-developed micro pore structure. The activation gas is usually CO₂, since it is clean, easy to handle and it facilitates control of the activation process because of the slow reaction rate at temperatures around 800 °C (Zhang et al., 2004). On the other hand, the chemical activation process, carbonization and activation are carried out simultaneously. Chemical activation needs chemical activated agent as ZnCl₂, KOH, NaOH, H₃PO₄, or K₂CO₃ followed by heating under a nitrogen flow at temperatures in the range of 450–900 °C, depending on the activated agent used (Kayode and Olugbenga, 2015). The present work reviews and evaluates literature that focuses on the optimum conditions for the preparation of AC through recycling of date seeds material that is widely available in Middle East and South Africa countries via physical and chemical methods.

Carbon adsorption has numerous applications in removing pollutants e.g. color water streams both in the field and in industrial processes such as spill cleanup, groundwater remediation and drinking water filtration. However, its application fields are restricted due to high cost. Discharge of dyes in to effluents affects the people who may use these effluents for living purposes such as washing, bathing and drinking (Kayode and Olugbenga, 2015). The conversion of waste materials, agriculture by-products, and industrial by-products into ACs would add considerable economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbon (CAC), The present work deals with preparation of date seeds active carbon (DSAC) as agriculture by-products, and coke breeze active carbon (CBAC) as industrial by-products, and verify their efficiency in removal of Cadmium from aqueous solutions and compare the results obtained from two residual and show the best one. Batch adsorption experiments were utilized to study the metal removal efficiency using the selected sorbent material. The effect of various parameters such as contact time, initial metal concentration, pH, adsorbent mass, and

temperature upon the removal of cadmium were investigated, and the kinetics of the process were elucidated. The experimental data obtained were fitted to Langmuir and Freundlich models to analyze the adsorption equilibrium.

II. MATERIALS AND METHODS

Coke breeze is by-product of metallurgical industry was obtained from iron and steel Company for Environmental Waste Treatment, Egypt. Date seeds is agricultural by-product were brought from the local market in Egypt. And all other chemicals, such as NaOH and HCl, were laboratory grade. The instruments used for DSAC and CBAC preparation were: muffle furnace (Nabertherm more than heat 30-3000 °C), conductivity meter, desiccator, and digital magnetic stirrer, Shaker, Metal standards and concentrations were quantified using Atomic Absorption Spectrophotometer. Filter papers were used to remove the AC from the solution before determining the absorbance from the spectrophotometer. The standard test method ASTM-D3838 -80 was used (ASTM, 1996) to determine the pH of AC by using pH meter).

2.1. Sorbent Materials

DS and CB are used for the preparation of AC according to the research the following method were followed (Suresh et al., 2012).

2.1.1. Biomass

Before use, date seeds and coke breeze were washed several times with distilled water and left to dry in oven at 105°C, and then it was cut into small pieces, grained and sieved to an average particle size (2-3 mm) and were stored in a desiccator for further use (Suresh et al., 2012).

2.1.2 Carbonization and activation

The raw material was subjected to chemical treatment followed by pyrolysis. The activation was carried out by impregnation of both coke breeze and date seeds samples with phosphoric acid in a ratio of 1:2 (w/w) for 24 h, and then washed with distilled water several times until pH reached 4. After that, the samples were dried at 100 °C then pyrolysed in a muffle furnace in absence of air at 400-600 °C for 2 h. After pyrolysis, the resulting samples were washed with distilled water until the pH of the washing solution reached 6–7. The activated carbon samples were dried at 100 °C and kept dry till use. Both coke breeze and date seeds were kept in a desiccator and were used as is.

2.1.3. Chemical characteristics

The chemical characteristics of activated date seeds (DSAC) and coke breeze (CBAC) are as follows (The coke breeze which used contain 90.6 % fixed carbon, 1.16% volatile matter, 8.24% ash, 1.11 % and 0.75 humidity. The coke breeze fines used in this work have size less than 0.3 mm. and date seeds carbon content 36.56 wt. % and ash content 64.97 wt. %).

2.1.4. Reagents and chemicals

All reagents and chemicals used were of analytical reagent grade. Stock solution of 1000 ppm cadmium was prepared from reagent grade (Imperial Chemicals) by dissolving the required mass in 1 L of double distilled water. This solution was used to obtain diluted metal ion solutions as required.

Metal standards and concentration were quantified using Atomic Absorption Spectrophotometer (Varian Spectra AA, Australia).

2.3. Batch Adsorption Processes

Batch adsorption experiments were carried out in a thermo stated water bath/shaker at a constant shaking rate. The effect of concentration of cadmium in solution, adsorbent dose, time of adsorption and temperature were studied. 25 mL of cadmium solution of known concentration (20- 200 mg/L) were shaken with different weights of adsorbent material (0.5- 3. g/l) at different temperatures (20- 45°C), for mixing time (2 hr.) and throughout the pH of 6. Separation of the solid phase from liquid was achieved first by centrifuging for 10-15 min (4000 rpm) and was followed by filtration. The filtrates were analyzed for the remaining cadmium ion concentration. spectrophotometrically at 445 nm (Jenway 6350 UV-Visible Spectrophotometer) using dimethylglyoxime method (APHA, 1985)

The % of metal ion removal was calculated as follows:

$$\% \text{ removal} = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (1)$$

Where C_0 and C_t are the initial and final concentration of metal ions in solution (mg/L or ppm), respectively.

The amount of metal ion accumulated per unit mass of adsorbent was evaluated using the following equation (Kawthar et al., 2017, Chuah et al., 2005- Al-Muhtaseb et al., 2008- Genc et al., 2007- Volesky, 2007):

$$q_t = (C_0 - C_t) V / m \quad (2)$$

Where m is the weight of sorbent used (g) and V is the volume of metal solution (L). At equilibrium contact time t_e , C_t becomes C_e and the amount of metal ion sorbed (q_t)

III. RESULTS AND DISCUSSION

3.1. Effect of Adsorbent Weight

The effect of various weights of AC i.e. 0.5,1,1.5,2,2.5, and 3 g/l of CBAC and DSAC separately upon the cadmium removal from solution and adsorption capacity (where concentration of cadmium ion is 100mg/l, at pH (6) and agitation time of treatment 2 hr with a rotating shaking 200RPM at room temperature) is shown in figure 1 and 2. The results indicated that cadmium removal % increased as the weights of both CBAC and DSAC increase. The removal of cadmium reached 98.43% and 98.74% when using CBAC and DSAC respectively. This may attributed to the fact that increasing the adsorbent amount increased the surface area available for more metal ion adsorption. (Chuah et al., 2005- Ebaid and, El-Refae, 2007). The optimum ACs dosage was at 3 g/l. It is because of the increasing the available overall surface area of the ACs. The change of adsorption capacity rate might be due to fact that at first all the adsorbent sites are available and cadmium concentration is very high in the solution. Later, adsorption rate was lowered which indicates the possible monolayer formation of cadmium on the ACs surfaces (Ahmed et. al., 2009). That may be to the lack of available active sites required for further uptake after reaching the equilibrium (Sha et al., 2010).

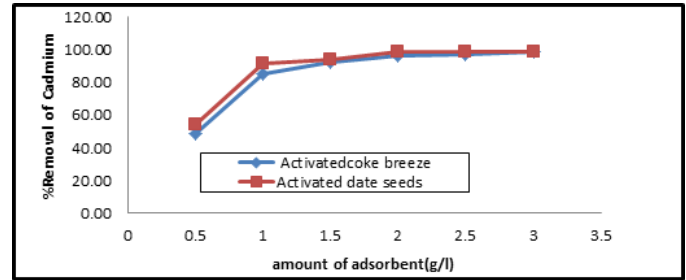


Fig. 1. The effect of the amount of activated carbon of (coke breeze and date seeds) on cadmium removal.

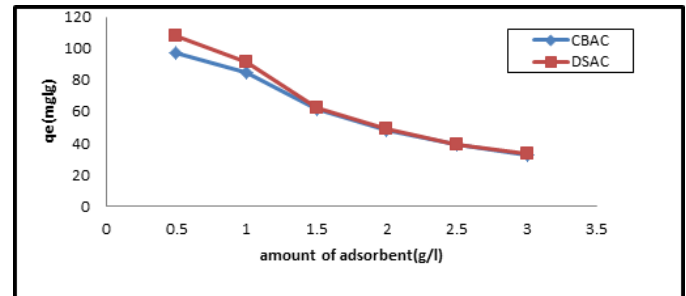


Fig. 2. The effect of the amount of activated carbon of (coke breeze and date seeds) on removal capacity of cadmium.

3.2. Effect of Temperature

The relation between cadmium removal at different temperature range from 20 to 40 °C is illustrated in figure 3. (Where the concentration of cadmium ion is 100mg/l, at pH (6) and 1g/ l adsorbent material and contact time 2 hr.). The figure show that % removal of Cd^{+2} at (20-40°C) are (85-99.47, 80.25-93.56) in case of CBAC and DSAC respectively. it is clear that the adsorption rate increased as the temperature increased. The increase of adsorption percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of adsorption rate, also the raise of temperature leads to an increase of the rate of mass transfer of the diffusion and rat of adsorption (Sayed et al., 2001 and Sayed et al., 2002). And this increase in adsorption indicates that the process is endothermic and that the rise in temperature favored the adsorbate transport within the pores of the adsorbent. This increase in sorption may be diffusion controlled (Bansal et al., 2009). From the above we found the optimum temperature for removal at 40°C for both AC.

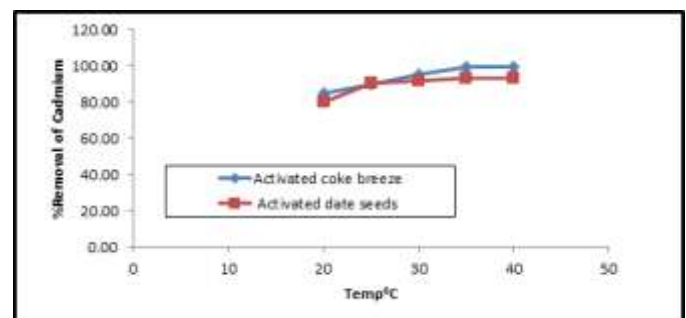


Fig. 3. The relation between temperature and cadmium removal by activated carbon of (coke breeze and date seeds).

3.3. Effect of Initial Cadmium Concentration

Figure 4 reveals the effect of the initial cadmium concentration from 50 to 200 mg/l, at pH6 and dose of CBAC and DSAC is 1g/l and contact time 2 hr. From which it is clear that the amount of cadmium removal decreased for both sorbent materials employed as the amount of cadmium increased. As well, the maximum metal removal % obtained using both CBAC and DSAC was achieved 97.33% and 100% respectively at 50mg/l. This is attributed to the availability of more adsorption sites at low metal ion concentrations. (Bansal et al., 2009) also reported that at the equilibrium time of 120 min was the time at which most of the surface sites were exhausted and that repulsive forces between solute molecules and bulk phase were becoming more dominant. The ability of CBAC and DSAC to adsorb cadmium decreased at concentrations higher than 50mg/l, 2 hour contact time because binding of function groups on the surface of ACs and cadmium was weak because the longer the contact time of adsorption, the more collision between particle of ACs and cadmium appeared (Xian-lun Deng et al., 2016) The optimum concentration for removing cadmium at concentrations 50mg/l for both AC.

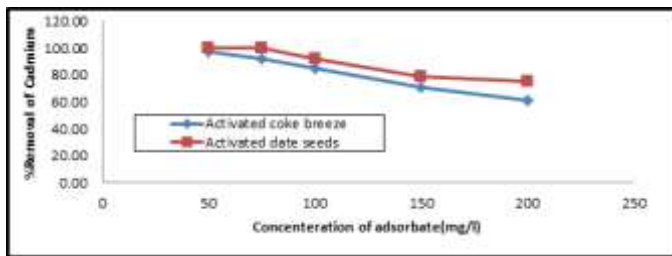


Fig. 4. Effect of initial cadmium concentration on removal of cadmium using Activated carbon of (coke breeze and date seeds).

3.4. Effect of Agitation Time

The effect of agitation time upon the amount of cadmium adsorbed using fixed activated weight carbon of coke breeze and weight carbon of activated carbon of date seeds are shown in Figure 5. From these figures it is clear that the maximum amount of cadmium adsorbed sharply during first 20 min. after that period adsorption slowed down. Adsorption of 91.55 and 85% Cd⁺² for activated date seed and activated coke breeze was achieved after 2hr. the adsorption of Cd⁺² was also found depend on pore volumes and internal surface areas of the derived activated carbons. Here also, the adsorption performance of the activated carbons increased with the duration of activation. Again, this can be attributed to the increase in their surface area and pore volumes with increase in activation time (William et al., 2016). Maximum adsorption obtained at 2hr at which most of the surface sites were exhausted and that repulsive forces between solute molecules and bulk phase were becoming more dominant. (Bansal et al., 2009).

3.5. Effect of pH

The pH of the solution was reported to be one of the important controlling parameters for metal sorption on biomass (Pandey et al., 2007, Aslam et al., 2010). As well,

variation in pH was reported to change not only the characteristics and availability of metal ions in solution but also the chemical status of the functional groups responsible for biosorption (Blázquez et al., 2005). Figure 6 show the influence of pH on the adsorption of cadmium onto activated carbon of coke breeze and activated carbon of date seeds. The results indicated that higher cadmium% removal at pH 6.

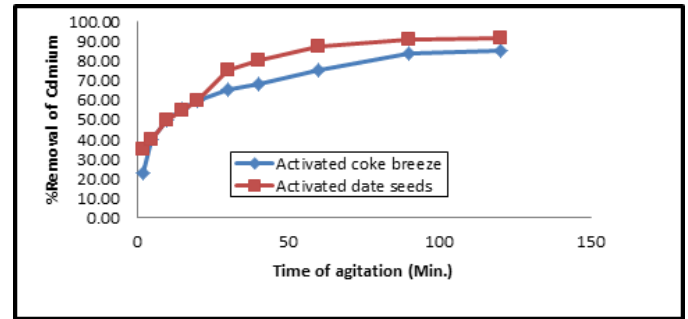


Fig. 5. Effect agitation time on removal of cadmium using activated carbon of coke breeze and date seeds.

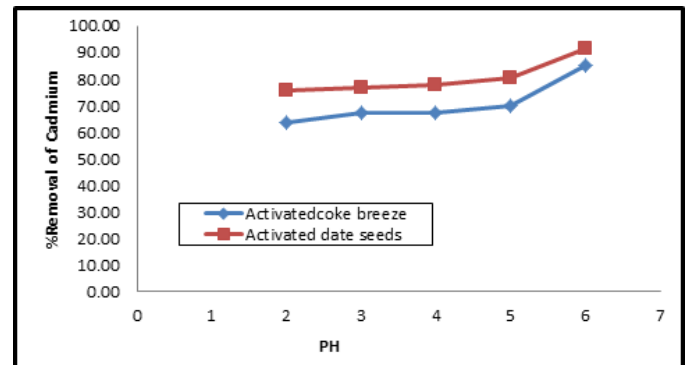


Fig. 6. The effect of varying the pH upon the amount of cadmium adsorbed (mg/l) at time=120 min using activated carbon of coke breeze(1g/l) and date seeds.

3.6. Adsorption Kinetics

Numerous kinetic models have been used to describe the reaction order of adsorption systems based on solution concentration (Sud, et al. 2008,). To test the experimental data obtained, two different kinetic models were used, namely: the pseudo-first-order and pseudo-second-order Lagergren equations (Lagergren, and Svenska, 1898). For the pseudo-first order rate, the equation used was present in Figure 7.

$$\log (q_e - q_t) = \log (q_e) - k_1 t/2 \quad (3)$$

Where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t , respectively. The rate constant k_1 (min^{-1}) for the pseudo-first-order sorption, A linear graph with negative slope is expected from the plot of $\ln (q_e - q_t)$ against t , k_1 and q_{cal} can then be obtained from the slope and intercept respectively showed in table 1.

The equation used for pseudo second-order rate was (Ho, and McKay, 1999).

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where K_2 is the rate constant of the pseudo-second-order kinetic equation in g/mg min^{-1} , q_e is the maximum sorption capacity in mg/g and q_t (mg/g) is the amount of sorption at time t . Linear graphs are obtained from a plot of t/q_t against t

from which q_e and k_2 can be calculated from the slope and intercepts as shown in table 1. Investigations of the use of CBAC and DSAC as sorbent for divalent Cd ion removal solution indicated that the process was a second order process showed in Figure 8.

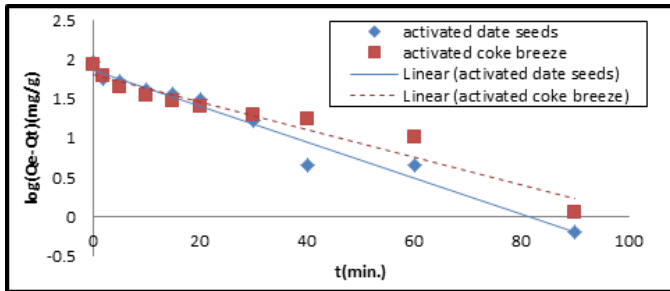


Fig. 7. The pseudo-first order rate, the equation for adsorption by activated coke breeze and activated date seeds

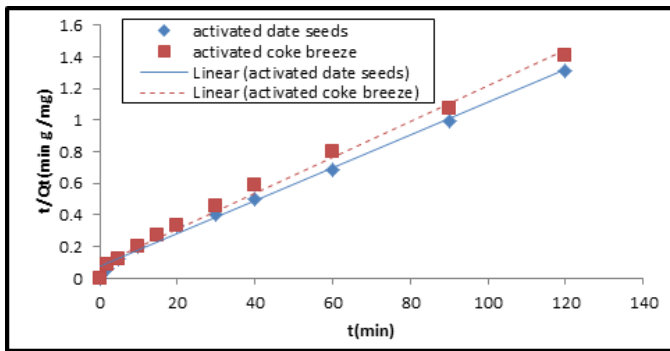


Fig. 8. The pseudo-second order rate, for adsorption by activated coke breeze and activated date seeds

The intraparticle diffusion model by Weber and Morris (W.J. Weber, J.C., 1963). Morris expressed by mathematical relation in Eq.(5);

$$q_t = K_{diff} t^{1/2} + C \quad (5)$$

where q_t ($mg\ g^{-1}$) is the amount of cadmium adsorbed at time t and K_{diff} ($mg\ g^{-1}\ min^{-1/2}$) is the rate constant for intra-particle diffusion. Insight into the thickness of the boundary layer can be obtained from the value of C , large intercept suggests great boundary layer effect. A plot of q_t versus $t^{0.5}$ can give a linear

or multilinear suggesting that intra-particle diffusion is involved in the adsorption process or two or more steps govern the adsorption process. However, if a linear graph is obtained and the plot passes through the origin then intra-particle diffusion is said to be the sole rate-limiting step. Figure 9 showed adsorption mechanism where A plot of q_t versus $t^{0.5}$ showed the correlation coefficients (R^2) were found to be 0.9159, and 0.9019 for DSAC and CBAC respectively, and corresponding values of intra-particle diffusion rate constant were 6.4873 , and $5.9215\ mg\cdot g^{-1}\cdot min^{-1/2}$ for DSAC, and CBAC, respectively. The values of rate constants and correlation coefficients for model are shown in Table 1. Lower and higher value of K_{diff} may indicate an enhancement of the rate of adsorption and better adsorption with improved bonding between pollutant and adsorbent particles (Lakshmi et.al., 2013), As well, the values of C obtained may provide an idea about the thickness of the boundary layer, i.e. the larger the intercept, the greater the boundary layer effect as well if the intercept = 0, intraparticle adsorption is the controlling mechanism (Mane et al., 2007). A linear portion represents a gradual adsorption stage with intra-particle diffusion contributing to molecules uptake (Kumar et al., 2010). The results in Table 1 indicate that the process of Cd adsorption onto both CBAC, and DSAC may be considered second-order reaction that involves to some extent intraparticle diffusion; however, the latter may not be the rate-limiting mechanism of the process. As the linear portion of curve doesn't pass through the origin (Yacouba et al., 2016).

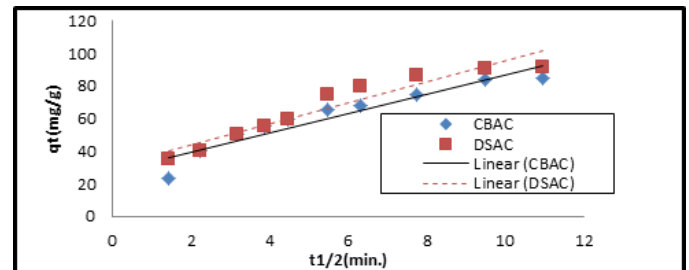


Fig. 9. (adsorption mechanism) Intra-particle diffusion of Cd²⁺ adsorption onto CBAC and DSAC.

TABLE 1. Kinetic parameters calculated for the sorption of cadmium onto CBAC and DSAC.

AC	Peseudo-first-order				Peseudo-second-order				Intra-particle diffusion		
	$K_1(\min^{-1})$	$q_{e,calc}(mg/g)$	$q_{e,exp}(mg/g)$	R^2	$K_2(g/mg.min)$	$q_{e,calc}(mg/g)$	$q_{e,exp}(mg/g)$	R^2	$k_i(mg/g.min^{1/2})$	C	R^2
CBAC	-.04053	6.153986	85	0.9428	0.001542	88.49558	85	0.9921	5.9215	27.949	0.9019
DSAC	-.050251	6.450773	91.55	0.9656	0.001456	96.15385	91.55	0.9924	6.4873	30.67	0.9159

3.7. Adsorption Isotherms

Sorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium (Sud et al., 2008). Both Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and mono component adsorption of metal ions by different sorbent materials. In the current study, the Langmuir and Freundlich isotherms were used to interpret the sorption equilibrium data. The linear equation for Freundlich isotherm applied was (Gupta et al 2003, Genc et al2007):

$$\log q_e = \log K_f + 1/n \log C_e \quad (6)$$

where K_f is correlated with the quantity of sorbate associated with the sorbent, and n is the Freundlich isotherm constant related to the strength of the sorption. Freundlich isotherm model is based upon the assumption that sorption occurs on heterogeneous surfaces and K_f may be useful for the evaluation of the adsorption capacity of metal ions in dilute solutions. The Freundlich constants (K_f and n) relate to sorption capacity and sorption intensity of the sorbent, respectively, and K_f is a useful for the evaluation of the adsorption capacity of metal ions in dilute solutions (Kandah

et al., 2010), as the larger values obtained indicate the higher adsorption capacity. As well, the magnitude of n gives an indication of the favorability of adsorption. In other words, if the value obtained are within the range of 2–10 it indicates a good adsorption characteristic, while values between 1 and 2 reflect moderately difficult and less than 1 have poor adsorption characteristic. As well, $1/n$ values obtained between $(0 < 1/n < 1)$ may signify that the surface of the sorbent was heterogeneous (El-Dars et.al.,2014) A plot of $\log q_e$ vs. $\log C_e$ for CBAC and DSAC are provided in Figure10, and the values obtained for the slopes and intercepts of these plots are presented in Table 2. Based upon the correlation coefficient and the value of n , it may be concluded that the experimental data better fitted the Freundlich model for CBAC as it has higher regression value of R^2 than that of DSAC. However, the magnitude of n for both CBAC and DSAC the range 2–10 which indicates a favorable process. The Langmuir isotherm utilized for the sorption equilibrium of CBAC and DSAC was:

$$C_e/q_e = 1/b Q_0 + C_e/Q_0 \quad (7)$$

where Q_0 and b are the Langmuir constants related to monolayer sorption capacity, and free energy of sorption, respectively. A plot of C_e/q_e vs. C_e is shown in Figure 11 and the values obtained for the slopes and intercepts of these plots are presented in Table 2. Essentially, the Langmuir treatment

is based upon the assumption that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface where the energy of adsorption is constant, and no transmigration of adsorbate into the plane of the surface may occur. The Langmuir constant b reflects quantitatively the affinity between the adsorbent and adsorbate, and the lower the value obtained the more affinity of metal to adsorbent material. In addition, the adsorption capacity may indicate the correlation between the variation of surface area and porosity of the adsorbent, i.e. the higher the surface area and pore volume provide for a higher capacity of metal ion adsorption (El-Dars et al., 2016). The dimensionless constant separation factor of the Langmuir isotherm can be expressed in terms of an equilibrium parameter R_L , which is defined as:

$$R_L = 1/(1+bC_0) \quad (8)$$

There are four probabilities for the value of R_L : for favorable adsorption $0 < R_L < 1$; for unfavorable adsorption $R_L > 1$; for linear adsorption $R_L = 1$, and for irreversible adsorption $R_L = 0$. In this study, the values for R_L obtained for the studied system indicate the favorability of Cd^{+2} adsorption onto both CBAC and DSAC. Moreover, the obtained R^2 value for the CBAC=0.9978 which indicates a better fit of the analytical for ACs with the Langmuir model and that may be indicative of a chemisorption process.

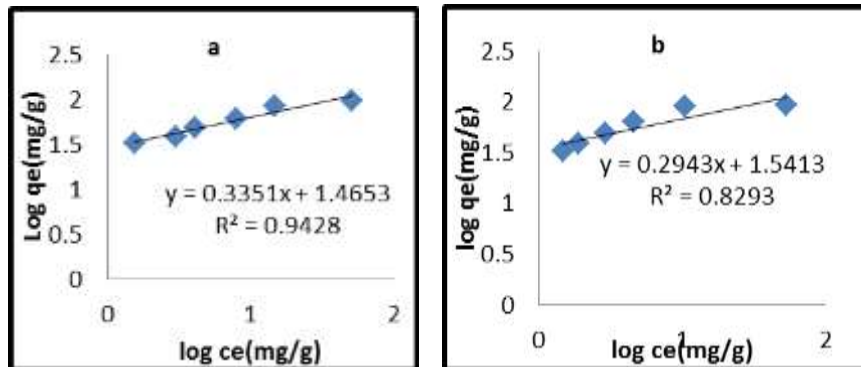


Fig. 10. Freundlich isotherm for Cd^{+2} adsorption onto activated coke breeze (a) and activated date seeds (b).

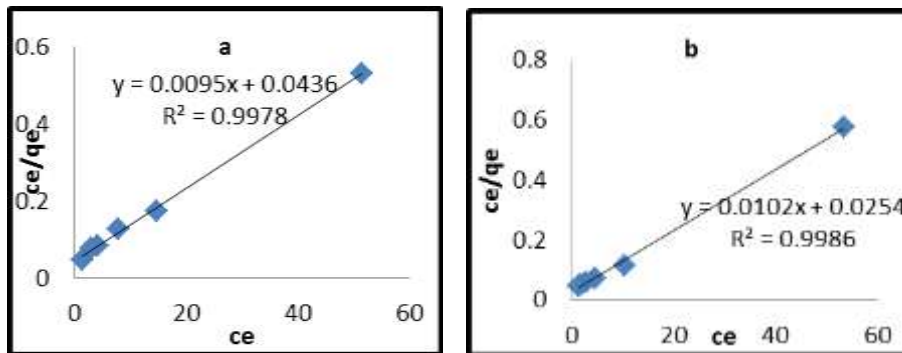


Fig. 11. Langmuir isotherm for Cd^{+2} adsorption onto coke breeze (a) and activated date seeds (b).

TABLE 2. Freundlich and Langmuir isotherm constants for Cd^{+2} adsorption

AC	Freundlich isotherm					Langmuir isotherm			
	Log K_f	k_f	1/n	n	R^2	$q_{max}(mg/g)$	1/ $q_{max}(g/mg)$	R_L	R^2
CBAC	1.6029	40.07744	0.2864	3.49162	0.9428	109.8901	0.0091	0.037139	0.9978
DSAC	1.5687	37.04248	0.3132	3.192848	0.8868	114.9425	0.0087	0.028909	0.9986

IV. CONCLUSION

The adsorption of Cd²⁺ from liquid solutions onto activated carbon from agricultural and industrial wastes from date seeds and coke breeze respectively using phosphoric acid as (H₃PO₄) as activated agent, has been investigated in the current study. The process was studied in a batch system with respect to the initial pH, contact time, temperature, adsorbent doses and cadmium initial concentration. The results showed that the optimum condition for cadmium removal are at PH6, cadmium initial concentration at 50mg/l, 40°C, and contact time is 2 hr for DSAC and CBAC but the efficiency of cadmium removal in case of using DSAC is higher than that of CBAC. All adsorption data from CBAC and DSAC are best fits with both Langmuir and Freundlich isotherms in batch experiments but favours Langmuir isotherm due to high regression. The results showed that the experimental data were well represented by pseudo-second order model. The results also indicated that process of Cd uptake by Coke breeze and date seeds were physical adsorption process. As the adsorbent is discarded as agricultural and industrial wastes, the treatment method is expected to be economical and environmentally feasible.

REFERENCES

- [1] A. Kumar, B. Prasad, I.M. Mishra, Isotherm and kinetics study for acrylic acid removal using powdered activated carbon, *J. Hazard. Mater.* 176, (2010) 774–783.
- [2] Al-Muhtaseb S. A., El-Naas M. H., Abdallah S., Removal of aluminum from aqueous solutions by adsorption on date-pit and BDH activated carbons. *Journal of Hazardous Materials* –(2008)-158 – P. 300–307.
- [3] American Public Health Association (APHA). *Standard Methods for Examination of Water and Wastewater* (18th edition). Washington D.C., USA. American Public Health Association- (1985).
- [4] Amin N, Hussain A, Alamzeb S, Begum S , Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children, district Mardan, Pakistan. *Food Chem* 136(3–4), (2013), P.1515–1523.
- [5] Aslam M. Z., Ramzan N., Naveed S., Feroze N. , Removal of Nickel (II) from Aqueous Solution Via Carbonized date Pits and Carbonized Rice Husks, *J Chil. Chem. Soc.*-(2010)- 55-N 1-P. 81-84.
- [6] Ahmad Said .M, Supwatul Hakim and Yuli Rohyami., The Effect of Contact Time and pH on Methylene Blue Removal by Volcanic Ash. *Int'l Conference on Chemical, Biological, and Environmental Sciences*, (2014), (pp. 11-13).
- [7] ASTM. , American Society for Testing and Materials Annual Book of ASTM Standard. Philadelphia PA., (1996).
- [8] Bansal M., Singh D., Garg V.K., Rose P Use of agricultural waste for the removal of nickel ions from aqueous solutions: equilibrium and kinetics studies., *International Journal of Civil and Environmental Engineering*-(2009)- 1: 2- P. 108-114.
- [9] Blázquez G., Hernández F., Calero M., Ruiz-Núñez L. F. , *Process Biochemistry*-(2005)- 40 - P. 2649-2654.
- [10] B.S. Girgis, M.F. Ishak, Activated carbon from cotton stalks by impregnation with phosphoric acid, *Mater. Lett.* 39 (2) (1999), P. 107–114.
- [11] Chuah T.G., Jumasiah A., Azni I, Katayon S., Choong S.Y. T., Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination* (2005)-175-P. 305-316.
- [12] Ebaid R. A., El-Refaei I. S., Utilization of Rice Husk as an Organic Fertilizer to Improve Productivity and Water Use Efficiency in Rice Fields. 8th African Crop Science Society Conference, El-Minia, 27-31 October (2007), -8-p.1923.
- [13] Farida M.S.E. El-Dars, Marwa A.G. Elngar, Abdel-Rahim S.Th. , El-Hussiny N.A., Shalabi M.E.H., Kinetic of nickel (II) removal from aqueous solution using different particle size of water - cooled blast furnace slag, *Desalination and Water Treatment*, 54:3, (2014), P. 769–778.
- [14] El-Dars, F.M.S.E., Sayed A.-E.O., Salah B.A., Shalabi M.E.H., Removal of nickel(II) from aqueous solution via carbonized date pits and carbonized rice husks, *Eurasian Chem. Tech. J.* 13 (2011), P. 267–277.
- [15] Genç-Fuhrman H., Mikkelsen P. S., Ledin A. , Simultaneous Removal Of As, Cd, Cr, Cu, Ni And Zn From Stormwater: Experimental Comparison Of 11 Different Sorbents, *Water Research* – (2007)-41- P. 591 – 602.
- [16] Gupta, V.K., Jain, C.K., Ali, I., Sharma, M. And Saini, V.K. , Removal Of Cadmium And Nickel From Wastewater Using Bagasse Fly Ash—A Sugar Industry Waste. *Water Research*, 37,(2003),P. 4038-4044.
- [17] Gilbert Rios , *Nanoporous Materials for Energy and Environment*, Hand Book, Pan Stnford(2012).
- [18] Guang-zhen Zhu, Xian-lun Deng, Min Hou , Kang Sun, Yan-ping Zhang , Ping Li , Fang-min Liang , Comparative study on characterization and adsorption properties of activated carbons by phosphoric acid activation from corncob and its acid and alkaline hydrolysis residues , *Fuel Processing Technology* 144 (2016) ,P.255–261
- [19] Haimour NM, Emeish S. Utilization of date stones for production of activated carbon using phosphoric acid. *Waste Manag* (2006), 26(6):651e60.
- [20] Hadoun H, Sadaoui Z, Souami N, Sahel D, Toumert I, Characterization of mesoporous carbon prepared from date stems by H₃PO₄ chemical activation, *Appl. Surf. Sci.* 280 (2013) P. 1–7.
- [21] John S, Santhi S (1994) Electroplated cobalt–cadmium selective solar absorbers. *Sol Energy Mater Sol Cells* 33(4):,(1994),505.
- [22] Xu J.Z., Chen L.Z., Qu H.Q., Jiao Y.H., Xie J.X., Xing G.G.. Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with H₃PO₄. *Appl. Surf. Sci.* 320 (2014), P. 674–680.
- [23] Lakshmi J., Vasudevan S., Graphene—A promising material for removal of perchlorate (ClO₄⁻) from water, *Environ. Sci. Pollut. Res.* 20 (2013) 5114–5124.
- [24] Suresh Kumar Reddy K, Ahmed Al Shoaibi, Srinivasakannan C., A comparison of microstructure and adsorption characteristics of activated carbons by CO₂ and H₃PO₄ activation from date palm pits. *New Carbon Materials*, (2012), P. 344–351. [https://doi.org/10.1016/S1872-5805\(12\)60020-1](https://doi.org/10.1016/S1872-5805(12)60020-1)
- [25] Kayode Adesina Adegoke, Olugbenga Solomon, Dye sequestration using agricultural wastes as adsorbents. *Water Resources and Industry*, (2015). <https://doi.org/10.1016/j.wri.2015.09.002>.
- [26] Kawthar Al-Balushi , Subramanyam Revanuru and Sreedhar Reddy Sajjala, Preparation of Activated Carbon from Date Seeds and Evaluation of Its Applications, *International Conference on Civil, Disaster Management and Environmental Sciences (CDMES-17)* Feb. 2-3, (2017)
- [27] Kandah M. I., Abu Al-Rub F. A., Bawarish L., Bawarish M., Al-Tamimi H., Khalil R., Sa'ada R. Adsorption of cadmium onto activated and non-activated date pits, *World Academy of Science, Engineering and Technology* – (2010) -62 – P. 204-208.
- [28] Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ Pollut* 152(3):(2008),P.686–692.
- [29] Kayode Adesina Adegoke, Olugbenga Solomon. (2015). Dye sequestration using agricultural wastes as adsorbents. *Water Resources and Industry*.
- [30] Lambert R, Grant C, Sauve S., Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. *Sci Total Environ* 378(3):(2007),P.293–305.
- [31] Martín M. I., López F. A., Pérez C., López-Delgado A., Alguacil F. J. Adsorption of heavy metals from aqueous solutions with by-products of the steelmaking industry, *J Chem. Technol Biotechnol-* (2005)- 80 – P.1223–1229.
- [32] Danish M., Hashim R, Ibrahim M.N.M., Sulaiman O., Effect of acidic activating agents on surface area and surface functional groups of activated carbons produced from Acacia mangium wood, *J. Anal. Appl. Pyrolysis* 104 (2013), P. 418–425.

- [33] Danish M., Hashim R., Ibrahim M.N.M., Sulaiman O, Optimized preparation for large surface area activated carbon from date (*Phoenix dactylifera* L.) stone biomass, *Biomass Bioenergy* 61 (2014), P. 167–178.
- [34] Benadjemia M, Millière L, Reinert L, Benderdouche N, Duclaux L, Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves, *Fuel Process. Technol.* 92 (6) (2011), P. 1203–1212.
- [35] Nahil MA, Williams P.T., Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks, *Biomass Bioenergy* 37 (2012), P. 142–149.
- [36] Nemr AE, Nemr O, El-Sikaily A, Khaled A., Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. *Journal of Hazardous Materials*, (2009), P.102–110.
- [37] Pandey P. K., Choubey S., Verma Y., Pandey M., Kamal S. S. K., Chandrashekhar K. , Int. J. Environ. Res. Public Health- (2007)-4 N 4- P.332-339.
- [38] Pereira R.G, Veloso C.M. , Silva N.M., Sousa L.F., Bonomo R.C.F., Souza A.O., Souza M.O.G., Fontan R.C.L, Preparation of activated carbons from cocoa shells and siriguela seeds using H₃PO₄ and ZnCl₂ as activating agents for BSA and α -lactalbumin adsorption, *Fuel Process. Technol.* 126 (2014),P. 476–486.
- [39] Sayed, S. A., Khalifa G. M. , El-Faramawy E. S. R. and Shalabi M. E. H., *Egyptian Journal Of Chemistry*, vol.45 No.1, (2002), pp. 47-66.
- [40] Sayed, S. A., Khalifa G. M. , El-Faramawy E. S. R. and Shalabi M. E. H., "VII International Mineral Processing Conference," Szczyrk, Poland, September 17-19, (2001).
- [41] Singh RP, Agrawal M., Variations in heavy metal accumulation, growth and yield of rice plants grown at different sewage sludge amendment rates. *Ecotoxicol Environ Saf*, (2010), 73(4):632–641.
- [42] Sud D., Mahajan G., Kaur M.P., Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a Review. *Bioresource Technology*- (2008)- 99-P. 6017–6027.
- [43] Lagergren S., Svenska B.K., On the theory of so-called adsorption of materials, *R. Swed. Acad. Sci. Doc Band*, 24 (1898), pp. 1-13.
- [44] Sha Liang et al., Isotherms, kinetics and thermodynamic studies of adsorption of Cu²⁺ from aqueous solutions by Mg²⁺/K⁺ type orange peel adsorbents. *Journal of Hazardous Materials*, (2010), P. 756–762.
- [45] T. Zhang et al. , Preparation of activated carbon from forest and agricultural residues through CO₂ activation,(2004),P. 53–59.
- [46] T. Vernersson, P.R. Bonelli, E.G. Cerrella, A.L. Cukierman, Arundo donax cane as a precursor for activated carbons preparation by phosphoric acid activation, *Bioresour. Technol.* 83 (2) (2002),P. 95–104.
- [47] T.H. Liou, Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation, *Chem. Eng. J.* 158 (2) (2010),P. 129–142.
- [48] Volesky B., Biosorption of heavy metals, *Water Research* –(2007)-41- P. 4017 – 4029.
- [49] V.S. Mane, I.D. Mall, V.C. Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, *J. Environ. Manage.* 84(4), (2007) 390–400.
- [50] Waalkes MP, Cadmium carcinogenesis in review. *J Inorg Biochem* 79(1–4), (2004),P.241–244.
- [51] Wang J., Chen C., *Biotechnology Advances* –(2009) – 27-P. 195–226.
- [52] William Buah1, Jennifer MacCarthy , Samuel Ndur, *International Journal of Environmental Protection and Policy*, Conversion of Corn Cobs Waste into Activated Carbons for Adsorption of Heavy Metals from Minerals Processing Wastewater, (2016); 4(4): 98-103.
- [53] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanitary Eng. Div. Am. Soc. Civil Eng.*, 89 (1963), pp. 31-59
- [54] W. Li, J.H. Peng, L.B. Zhang, H.Y. Xia, N. Li, K.B. Yang, X.Y. Zhu, Investigations on carbonization processes of plain tobacco stems and H₃PO₄-impregnated tobacco stems used for the preparation of activated carbons with H₃PO₄ activation, *Ind. Crop. Prod.* 28 (1) (2008), P. 73–80.
- [55] Y.Y. Sun, Q.Y. Yue, B.Y. Gao, L.H. Huang, X. Xu, Q. Li, Comparative study on characterization and adsorption properties of activated carbons with H₃PO₄ and H₄P₂O₇ activation employing *Cyperus alternifolius* as precursor, *Chem. Eng. J.* 181-182 (2012), P.790–797.
- [56] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Proc. Biochem.*, 34 (1999), pp. 451-465.
- [57] Yacouba SANOU, Samuel PARE, Gnon BABA, Nyonuwsro Kwamivi SEGBEAYA, Libona Yvonne Bonzi-Coulibaly, Removal of COD in Wastewaters by Activated Charcoal From Rice Husk, *RSE*, 12 September (2016).