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RESEARCH ARTICLE

Removal of Cadmium ions By Several Solid Stationary Phases Prepared from Papyrus Plant

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Abstract

The removal of Cd^{2+} ions from aqueous solution, has been done by using stationary phases prepared from papyrus plant. The dried (DP) treated with 0.036 M ethylene diamine tetra-acetic acid (EDTA) at pH=10, the activated carbon (AC) samples (SAC and PAC) were treated by chemical activation with sulfuric acid and phosphoric acid. Then activated carbon has been modified by nitric acid and gives the oxidized sulfuric activated carbon (OSAC) and oxidized phosphoric activated carbon (OPAC). Batch adsorption experiments were held at different pH values (2 - 6), contact time (5 - 300) min, initial metal concentration (25 - 300) mg/L, where the adsorbed dosage (25 - 200) mg, and solution temperature (298 - 318) K. The oxidized activated carbon, activated carbon and the dried from were seen as Fourier Transform Infrared (FTIR), as well as Scanning Electron Microscopy (SEM). The particular adsorption stability was described using Langmuir as well as Freundlich isotherm designs. The adsorption kinetics followed a pseudo-second get kinetic design and intra particle diffusion was involved in the adsorption procedure. Thermodynamic outcomes indicated how the adsorption procedure was quickly arranged and endothermic within nature.

INTRODUCTION

Cadmium inorganic pollutant with high toxicity which its emission sources are broadly diffused, giving rise to a pollution with wide environmental distribution. Because of this, environmental principles define severe limitations on the maximum cadmium concentration in natural water bodies besides the highest concentration allowed for wastewater discharge. In order to assure the obedience with those bounds, suitable technologies of depuration are usually required. There could be a removal for Cadmium by chemical precipitation, the exchange in ions, adsorption, electrochemical deposition, etc. (Letterman, 1999). Adsorption on granular activated carbon is a largely used method for removing organic pollutants. Applying it to metallic ions removal is a significant diffused, even though the removing competence for these substances is often less than it is for the organic ones**[1].** Papyrus plant is a water plant that belongs to the Cyprus family. It is a sustained plant, with evergreen growing groups in the edges of ponds. Papyrus breed through division by alrezumat under the surface of the water. It can grows (4 to 5 m) (13 to 16 ft.) high, Papyrus fiber contains 54 - 68% cellulose and 24 - 32% lignin**.** Having a large surface areas on activated carbons (AC) they could be used as adsorbent materials, microporous structures, high degree of surface motivates the capacities of adsorption [2]. However, commercially available activated carbons are not widely used because of the high cost due to the use of non-renewable and relatively high cost starting materials such as coal. But there are continuous efforts made by researchers in order to produce cheaper, with more impact, and is a friend to activated carbons in environment [3-6]. They have taken different approaches that include: using various precursors such as agricultural byproducts materials; using different chemicals for activation; and developing various methods of arrangements. Olive plant water hyacinth remains a raw material for producing activated carbon that is considered as among the best candidates of agricultural wastes as it has a cheap and quite abundant, particularly in the Mediterranean countries. The purpose of this study is to investigate removing cadmium from aqueous of samples using activated carbon prepared from papyrus plant. The effective parameters on absorption process like pH, contact time, initial concentration, adsorbent dose and temperature of metal ions were studied. Also the adsorption equilibriums were studied.

Experimental

2. Material and Method

2.1. Preparation of stationary phases

The roots of the papyrus plant was removed while the rest was washed using tap water, next using distilled normal water last but not least ended up being over loaded throughout 0. 025 M EDTA on pH 10 instantaneously with regard to eliminating any metal ions adsorbed within the papyrus plant last but not least rinsed using distilled normal water for a lot of occasions along with dry throughout the oven on 110 ºC with regard to 48 h next dry (DP) had been floor along with stashed throughout desiccators until finally utilized in adsorption trials. Activated carbon samples have been prepared in two forms; the first form SAC (sulfuric activated carbon) sample was prepared by soaking 200 g of dry plant in concentrated sulfuric acid at ratio 1: 3 (wt.: wt.) while (sp. gr . H_2SO_4 = 1.84). The second form sample was prepared in a similar way PAC (phosphoric activated carbon) by soaking 75 g of dried plant in concentrated phosphoric acid at ratio 1: 3 (wt.: wt.) while (sp. gr. H_3PO_4 = 1.88), both of the two samples in contact with the acid, at room temperature for 2 days. The two samples separately were treated by distilled water till it becomes free from any traces of H_2SO_4 or H_3PO_4. The washed 2 samples were dried at 110 ºC for 48 h, in addition to slipped into a muffle oven (in a stainless steel reactor) in which the materials were warmed gradually with absence of fresh air at 550 - 600 ºC for 4h. After chilling for you to space temperature, the particular initialized co2 obtained was rinsed totally together with distilled normal water till the pH in the supernatant become regular at concerning (pH=6). After that, the particular materials were dried at 110 ºC for 24 h**.** The detailed modification process conducted was as follow; first type sample preparation OSAC (oxidized sulfuric activated carbon) by taking 15 g of sample SAC (prepared already), and add 150 ml of concentrated nitric acid at ratio 1: 10 (wt.: v). The second type OPAC (oxidized phosphoric activated carbon) sample preparation by taking 20 g of sample PAC (prepared already), and add 200 ml of concentrated nitric acid at ratio 1: 3 (wt.: v). It was boiled for 4 h to improve the formation regarding functional groups, for instance carboxylic acids. The rest of the product was laundered along with distilled water till the pH on the supernatant grow to be steady from in relation to (pH =6). The oxidized AC turned by utilizing nitric acidity was then dried at 120 ºC. Finally. After modification with $HN0_3$, OSAC and OPAC were found to contain some acidic groups, several authors has proposed the formation of new functional groups such as anhydride, hydroxyl and aldehydes, …., giving a higher cation exchange capacity. The acidic groups increase significantly with the increment of the concentration of nitric acid during the treatment. The carboxylic groups of surface carbon play an important role in the adsorption process [7].

2.2. Adsorption Experiments

Batch adsorption experiments were carried out in which aliquots of 25 mL of Cd (II) solutions of known concentration were poured into beaker glasses (25 mL) containing accurately weighed amounts of the adsorbents. Effect of pH on the adsorption of Cd (II) was studied by varying the pH from 1.0 to 6.0 by using a pH meter (JENWAY- LTD Instrument, digital model 3310). Effect of concentration: 25 ml of metal ion solution was prepared in conical flask with metal ion concentration (5 - 100) mg/L with sample (SAC, PAC, OPAC, OSAC and DP) (5) – (300) mgL^{-1} and dose 25 mgL^{-1} and place them in the shaker. The temperature was maintained at 25˚C. Conducted a study of contact time when the limits of 5-300 min the different stages of equilibrium by sampling efficiency 30 min of (SAC) and 60 min of (DP, PAC, OPAC and OSAC). Effect of adsorbent dose ranged from 0.025 to 0.2 g per 25 mL of solutions of cadmium. The beaker glasses were shaken at 150 rpm using an electric shaker for a prescribed length of time to attain equilibrium at 293 K and 318 K separately. Using a spectrophotometer (Apye - Unicom UV100 -Visible Spectrophotometer) conducted read the absorbance. The amounts of metal ion removal by:

$$\%E = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

q_e is the amount of metal ion (mg/g). (C_o), (C_e) equilibrium cadmium solution con-cert of metal ion (mg/g), (V solution of volume), (m weight of stationary phases) (g).

Result and Discussion

3. Characterization of stationary phases

3.1. FTIR spectroscopy:

FTIR spectra had been documented between four thousand and (100) cm^{-1} employing a Mattson four thousand FTIR spectrometer. Discs had been served by first combining 1 mg dried up carbon trial together with (500) mg regarding KBr (merck pertaining to spectroscopy) within the agate mortar then pressing resulting mixture with (5) tone / cm^2 pertaining to (5) minutes and (10) tone / cm^2 pertaining to (5) min below vacuum.

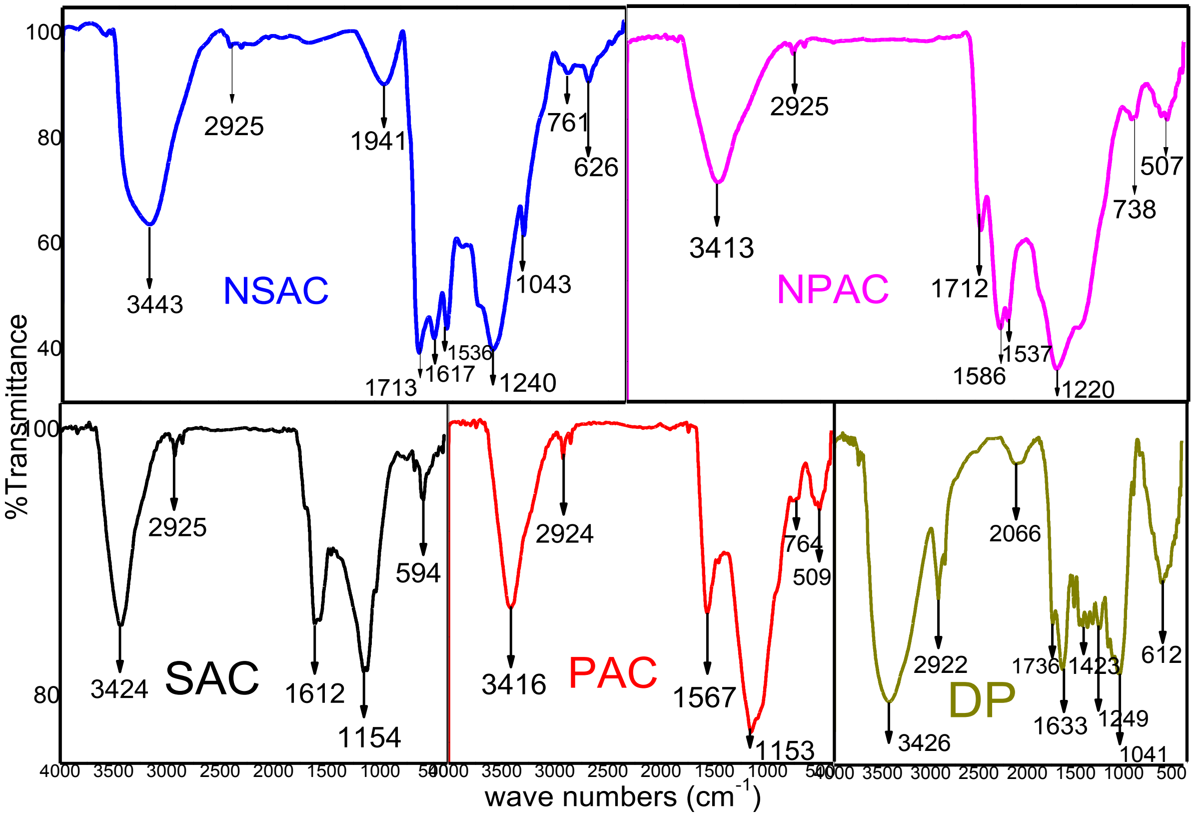

Fig (1): FTIR spectrum of oxidized activated carbon (OSAC, OPAC), activated Carbon (PAC, SAC) and dried (DP) papyrus plant.

Fig (1) shows FTIR spectra for samples (OSAC, OPAC, SAC, PAC and DP). Observation of the absorption bands show that the difference between activated carbon modified with nitric acid and non-modified activated carbon is mainly due to the formation of oxygen functionalities. All samples present vast ring from (3413-3443) cm^{-1} on account of O-H stretching out manner of hexagonal group along with adsorbed water. This shoulders discovered from (2922-2925) cm^{-1} on because of aliphatic (C-H) and appear for many samples [8]. Very small peak near (1712-1736) cm^{-1} is assigned to (C=O) stretching vibrations of ketones, aldehydes, lactones or carboxyl groups was observed in samples (OSAC, OPAC, DP) [9]. The bonds near (1633-1500) cm^{-1} is due to C=C elongating vibration in aromatic ring and is particularly witnessed for many materials. The weak intensity of this peak indicate that prepared activated carbon contain small amount of carboxyl group. The bonds near (1220-1240) cm^{-1} is due to C-O very obvious stretching vibrations of ethers for sample (OSAC, OPAC) .The broad absorption within the range (1300 -1000) cm^{-1} can be ascribed to various C-O bonds such as those in ethers, phenols ,alcohols and esters. The peaks observed around (610-875) cm^{-1} are attributed to in and out plane ring deformation in benzene derivatives. The HNO_3 treated carbon shows a significantly different trend in the FTIR spectra. Firstly, the appearance of a sharp absorption peak at (1612-1736) cm^{-1} indicates the abundant introduction of carboxylcarbonate structures. The bands at (1712-1713) cm^{-1} for OSAC and OPAC are because of elongating vibration connected with carboxyl groups for the ends connected with covering plane [10].

3.2. <u>Scanning electron microscopy (SEM):</u>

In order to know the structure sight of activated carbons, scanning electron microscopy (SEM) was generally employed to visualize sample morphology. Using scanning electron microscope (SEM; JSM, model 6510). Scanning electron microscopy of OSAC, OPAC, PAC, SAC and DP were obtained before the analysis, the materials were dry for 4 h at 110ºC. The edges of the double-sided tape were printed with gold. Micrographs were obtained in a secondary electron imaging mode using a potential difference of 30 KV. The micrographs obtained plainly reveal the actual porous composition connected with unique adsorbents from magnification of x1500 and x500 for (OSAC, OPAC, PAC, SAC and DP), respectively.

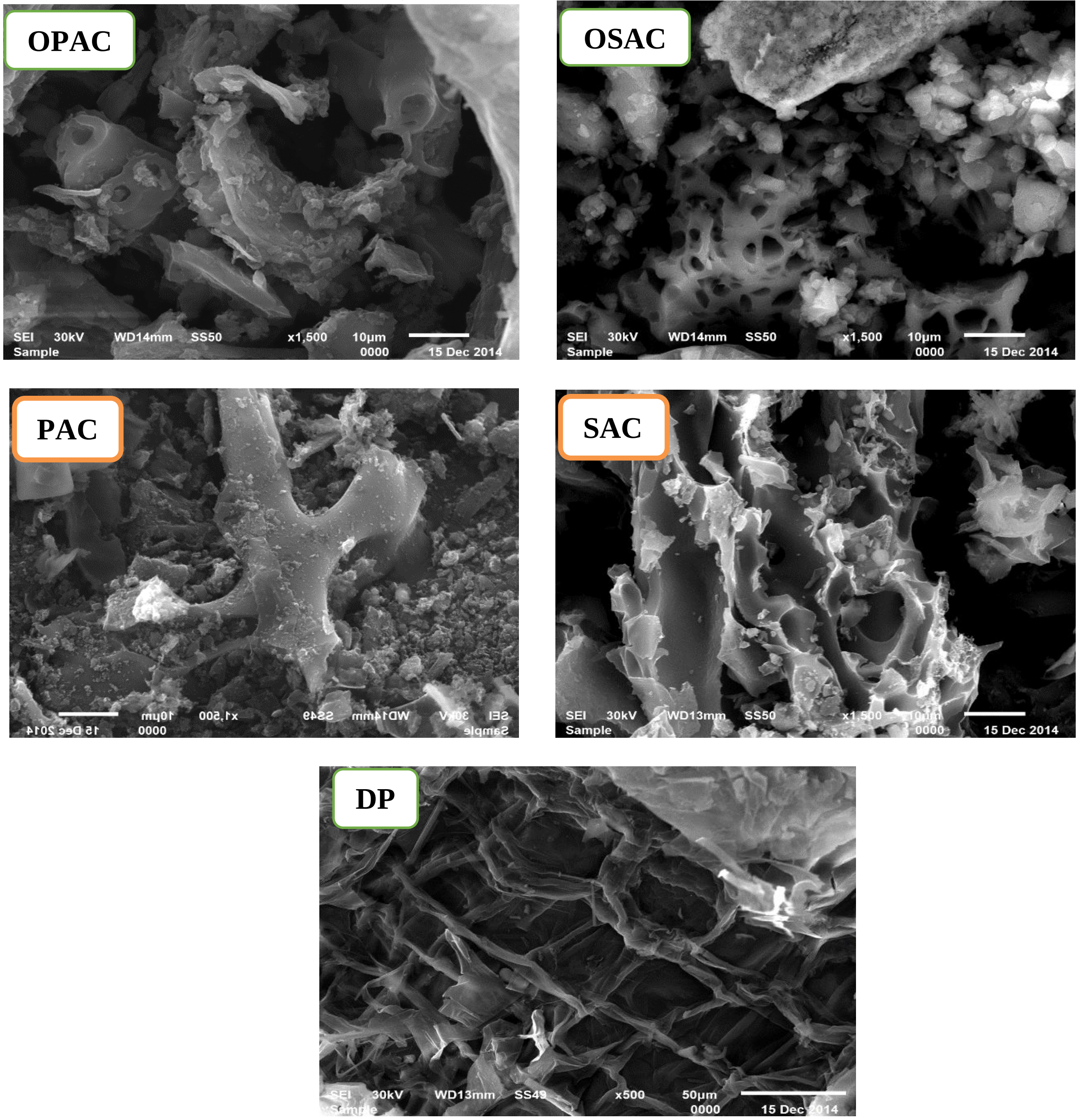

Fig (2): SEM photographs of OSAC, OPAC, PAC, SAC and DP.

3.3. pH effect on Cd^{2+} adsorption

The pH impact on the elimination of Cd^{2+} with SAC, DP, PAC, OPAC and OSAC, is shown in Fig (3) where the capacity of adsorption increases with the increasing of pH increases and the highest adsorption rate of Cd^{2+} happens on pH of 5. Though, the uptake capacity was not affected expressively by pH changing from 4.5 - 6 and the extraction effectiveness (% Extracted) is mostly retained fixed (variations was less than 3.5%). As pH increasing between pH=(2 – 5), The Cd^{2+} adsorbed quantity at equilibrium extracted (%) increases (17.67 - 39.75) % (SAC), (19.57 - 42.06) % (DP), (20.88 - 45.78) % (PAC), (23.09 - 61.04) % (OPAC) and (23.79 - 64.35) % (OSAC). SAC, DP, PAC, OPAC and OSAC comprises various functional groups that were influenced by changing the solutions pH. Consequently, through several pH valuations, electrostatic fascination forces plus the ionic components concerning ions of cadmium also varies stationary phases may be has a very energetic role during the adsorption procedure. At this point of research, at low pH values results indicated that, the decreasing of efficiency of cadmium removing could be an outcome of the cadmium (free Cd^{2+} ions) and ions of hydrogen competition on the sites of adsorption of varies adsorbents. Hydrogen Ions compete strongly in adsorption due to their small size. As values of pH increasing, the force of electrical repulsion declined and the cadmium ions may be related to the stationary phase surface besides affix to its surface. There was a competition between Cd^{2+} and other hydrogen ions for the sites of adsorption, which made it hard for Cd^{2+} to be present in the activated sites. Also, groups of carboxyl of adsorbents acquired the form of COOH not -COO-, which hindering the adsorption of Cd^{2+} onto the adsorbents. The same cases were attested in earlier researches for the adsorption of metal on different adsorbents [11, 12]. In case of DP the condensed volume of cadmium adsorption at pH more than 5 is perhaps because of the cadmium complexes formation with organic compounds obtained from the papyrus plant, which are in larger sizes than the free cadmium ions which weaken their adsorption competition. In addition, at pH valued more than 5.5, Cd $(OH)_2$ (poorly soluble) may be formed [13, 14] .

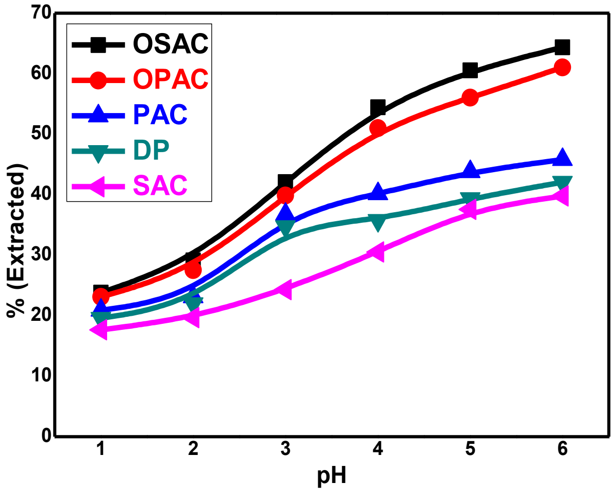

Fig (3): Effect of pH on adsorption capacity of Cd^{2+} by SAC, PAC, OSAC, OPAC and DP (Conditions: Con-cert= 100 mgL^{-1}, Temper=298K; Dose = 25 mg, V= 0.025 L).

3.4. Contact time effect on adsorption

The contact time effect on the capacity of adsorption of SAC, DP, PAC, OPAC and OSAC for Cd^{2+} are showed in Figure (4). It is clear in Figure (4) that the adsorption progression was very fast firstly, and then a great portion of the total metal quantity was detached after a limited minutes, higher than (40 - 45) % of volumes adsorbed of constant adsorbents with regard to Cd (II) occurred during 5 minute. With regard to PAC along with DP, beyond 57% happened within 5 min. for OSAC, OPAC and SAC. Which indicates that there were many empty sites of adsorption on the adsorbent surface existing at this phase, besides the excessive preliminary adsorption rate is caused by higher driving push concentration exposed to amount moved from the aqueous phase to the adsorbent active sites. Afterwards, rate of adsorption became sluggish close to the adsorption sense of balance and the best eradication associated with Compact Cd (II) transpired in(15-30) minute (SAC), (45-60) minute (DP, PAC, OPAC and OSAC). At that phase, the total amount of adsorbed metal onto the adsorbent was in an active equilibrium stage with the metal amount de-adsorbed. Time needed to achieve this level of balance was called the time of equilibrium also quantity of cadmium adsorb in the equilibriums times indicated the adsorbent maxi capacity of cadmium adsorb under these certain circumstances. Thus, 60 minutes is recognized as the equilibrium time of adsorption. To be definite, the enough time of contact was achieved, later tests of adsorption were prolonged to 5 hours.

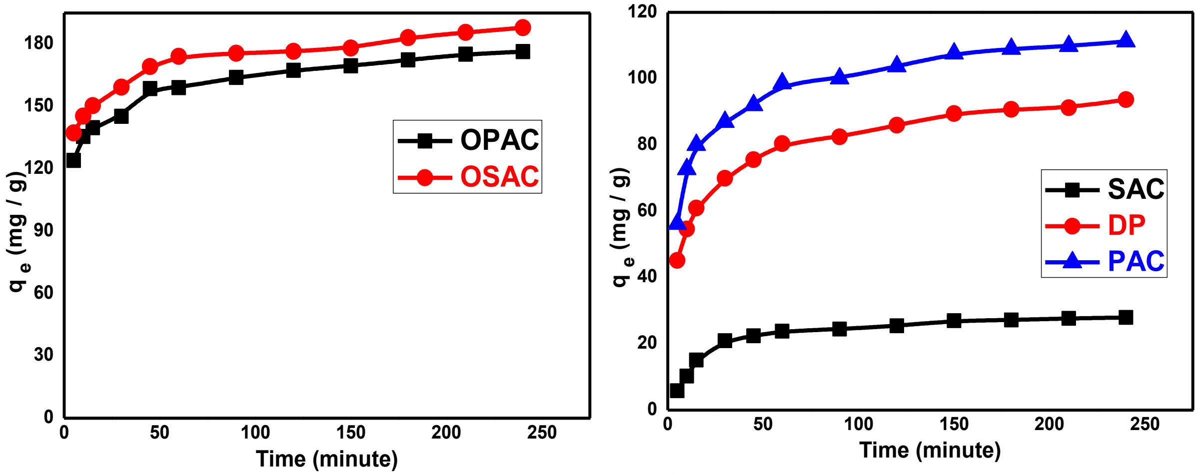

Fig (4): Effect of contact time on adsorption capacity of Cd^{2+}. (Conditions: C_o = 50 ppm (SAC), 150 ppm (DP, PAC) and 250 ppm (OSAC, OPAC), Temper=298K; dose = 25 mg, V= 250 mL).

3.5. Concentration effect on Cd^{2+}

The impact initial concentration on a removal of Cd^{2+} by SAC, DP, PAC, OPAC and OSAC were examined at optimum pH of 5 and at 25 °C, the results were graphed in Figure (5) presented these results. The capacities of equilibrium sorption of the sorbents boosts with the boost of the absorption of initial Cd^{2+}, during the introductory stages, the adsorption at variable absorptions is fast and decreases constantly during adsorption until the equilibrium is finally reached. The concluded fact out of this process is that, the higher absorption of initial Cd^{2+}, the more significant the gradient of driving force absorption at solid-liquid admix that leads to increasing the amount of Cd^{2+} adsorbed. When the preliminary concentration of Cd^{2+} rises (5 - 300) mg L^{-1} at room temperature, the quantity of Cd^{2+} adsorbed at equilibrium (q_e) rises (3.24 - 15.86) mg/g (SAC), (4.05 - 59.03) mg/g (DP), (4.24 - 64.05) mg/g (PAC), (4.60 - 86.64) mg/g (OPAC) and (4.77 - 111.74) mg/g (OSAC). While the extracted efficiency of cadmium decrease (72.38 - 31.72) % (SAC), (81.17 - 19.67) % (DP), (84.94 - 21.35) % (PAC), (92.06 - 28.88) % (OPAC) and (95.85 - 37.24) % (OSAC) .This decrease may be due to the blockage of papyrus plant (DP) (OH) and (oxidized AC) COOH group proved its function in heavy metals. Interactions between cadmium and cellulose's vicinal (OH and COOH) groups of DP and of oxidized AC have been advised. Most of these observations, along with the possible assigned functional groups at the FTIR spectra, confirm that the (OH and COOH) groups are principally liable for the extracted of Cd^{2+}using SAC, DP, PAC, OPAC and OSAC, together with COOH groups becoming accountable for a lot of the metallic uptake. It also shows that the maximum adsorption capacity of SAC is much lower than DP, and this is due to a main cause, which is the use of H_2SO_4 solution in AC pores that produced a drastic decrease on the surface area and in the micro-porosity of the material. It also affected the pore-size distribution in the mesopore and macropore ranges. This is caused by the ions of $HSO_4^-$and SO_4^{2-} which led to blocking the pores of AC [15].

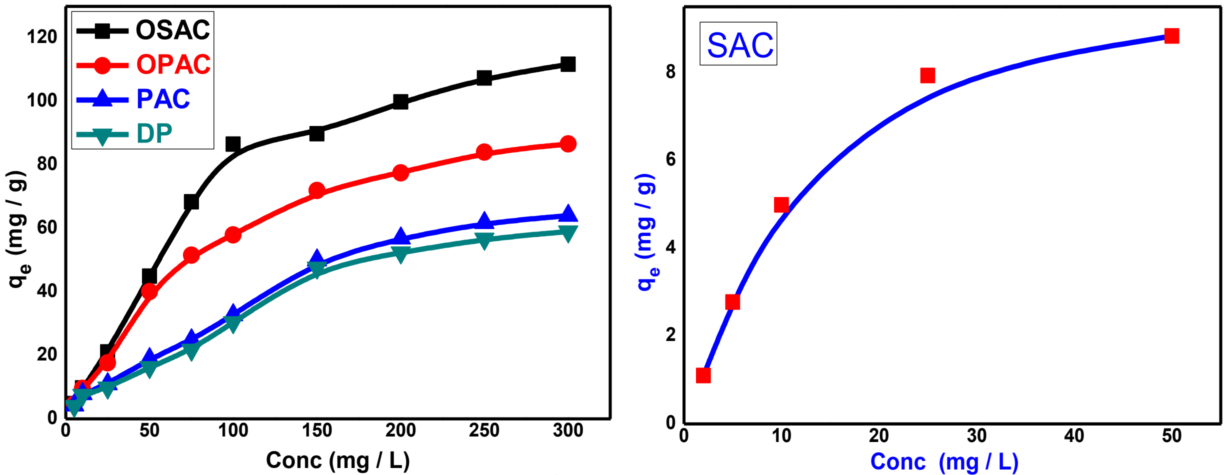

Fig (5): Concentration effect on the extracted of Cd^{2+} using SAC, PAC, OSAC, OPAC and DP. (Cond: Concern = (5)-(300) ppm, Temper=298 K; dose= 25 mg, V=0.025 L).

3.6 Temperature effect on adsorption of cadmium

The correlation between temperature and adsorption capacity of Cd^{2+} by SAC, PAC, OSAC, OPAC and DP is presented Fig (6). Table (1) shows that with increasing of temperature from 20 ° C to 45 ° C, the optimum adsorption amounts of Cd^{2+} (qe) using SAC, PAC, DP, OPAC and OSAC are increased from 15.86 to 21.08 mg g^{-1}, from 64.05 to 82.99 mg g^{-1}, from 59.03 to 82.88 mg g^{-1}, from 86.64 to 99.94 mg g^{-1} and from 111.74 to 124.54 mg g^{-1}, correspondingly. This is due to increasing of kinetic energy of Cd^{2+} as increasing in the temperature. Accordingly, the diffusion rate of Cd^{2+} ions across the outside boundary level in addition to in the central pores in varies adsorbents of which will increase along with temperature increasing, also quantity of Cd^{2+} up taking rises owing to pores size changing and the increasing of sorption sites number. Temperature Increasing will decrease the viscosity of the solution, leading to the increase in the rapid spread of metal particles in solution. In other words, the volume of adsorption increases when temperature of the adsorption process increases. It is clear that a physical adsorption is generally understood to be exothermic and the equilibrium adsorption will decrease with increase in the temperature of adsorption process [16]. An increase of the adsorption capacity with increase in the temperature indicates a significant adsorption being endothermic reaction [17].

Tab (1): Temperature effect on max of Cd^{2+} using OSAC, OPAC, PAC, DP and SAC.

Sample	q_e (mg/g)		
	25 ºC	35 ºC	45 ºC
OSAC	111.74	117.01	124.54

OPAC	86.64	93.92	99.94
PAC	64.05	76.85	82.12
DP	59.03	74.34	82.88
SAC	15.86	19.87	21.08

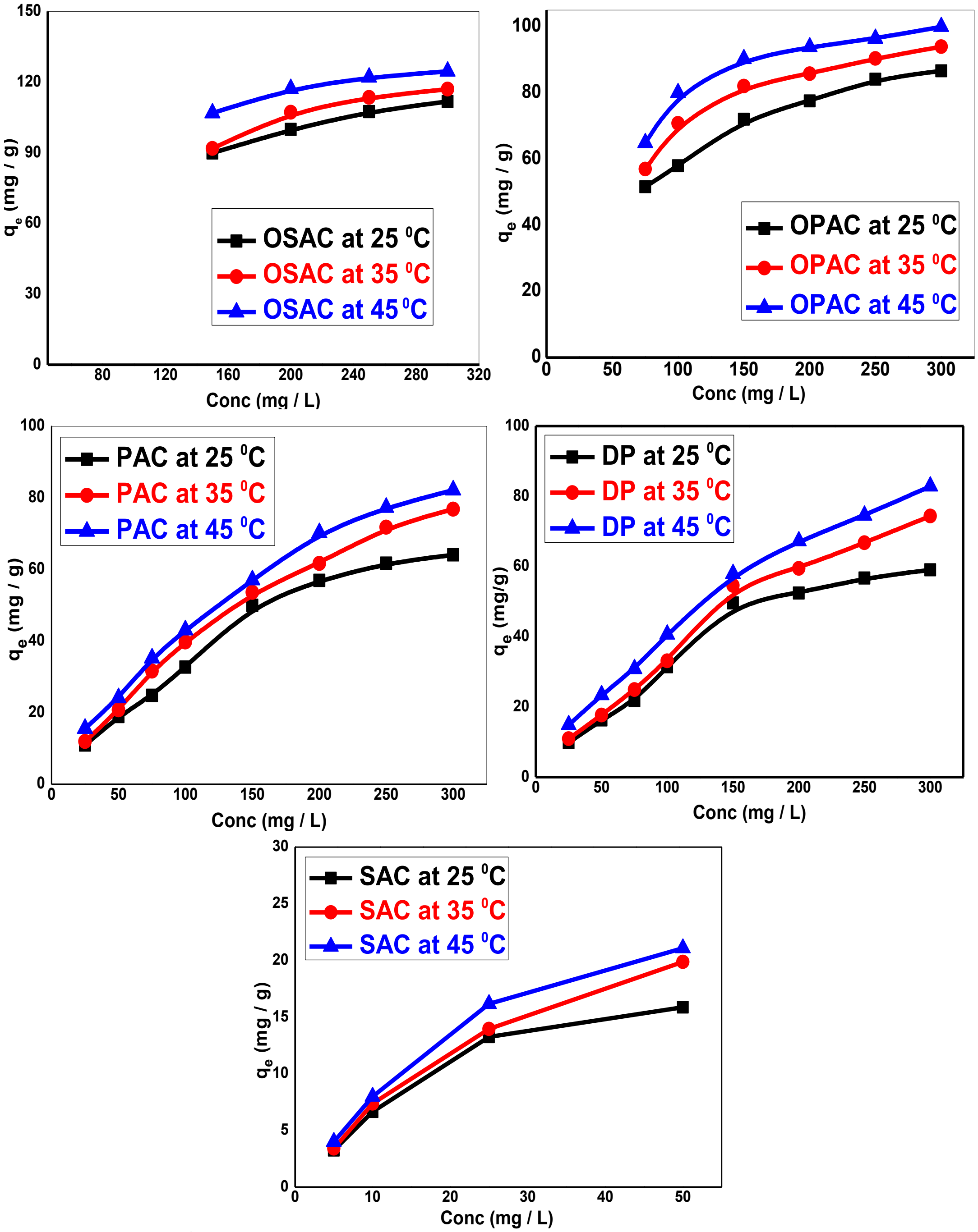

Fig (6): Temperature effect on Cd^{2+} using OSAC, OPAC, PAC, DP and SAC. (Conditions: C_o =5-300 mg/L; dose = 25 mg, V= 0.025 L).

3.7. Dosage effect

The dependency of Cd^{2+} removal on dose of SAC, PAC, OSAC, OPAC and DP is presented in Fig (7), it is clear that increasing the sorbent dose is on the side of Cd^{2+} elimination. With the increase of sorbent dose from (0.025 - 0.2) g, the percent of cadmium extracted (%) by SAC, DP, PAC, OPAC and OSAC increase (13.65 - 72.28) %, (15.26 - 75.1) %, (19.67 - 80.12) %, (18.84 - 48.12) % and (32.39 - 71.8) % respectively. This is due to the increasing of the sorbent surface area and the existence of more sites for sorption [18]. It is clear that increasing the adsorbent dose, leads to an increase in the efficiency of elimination, but there was a decrease in density of adsorption, the total quantity adsorbed for each unit mass. The decreasing density and increasing adsorbent dose is chiefly because of the particle interactions like the aggregation that results from increase in adsorbent concentration like aggregation could cause a reduction in the whole surface zone of the adsorbent. Clearly, the adsorbed of Cd^{2+} increase in region of OSAC > OPAC > PAC > DP > SAC under all conditions like concentration, temperature, pH and the dose of sorbent. This conduct is due to the increasing number of sites that are active on the adsorbents surface because of rising of adsorbents amount.

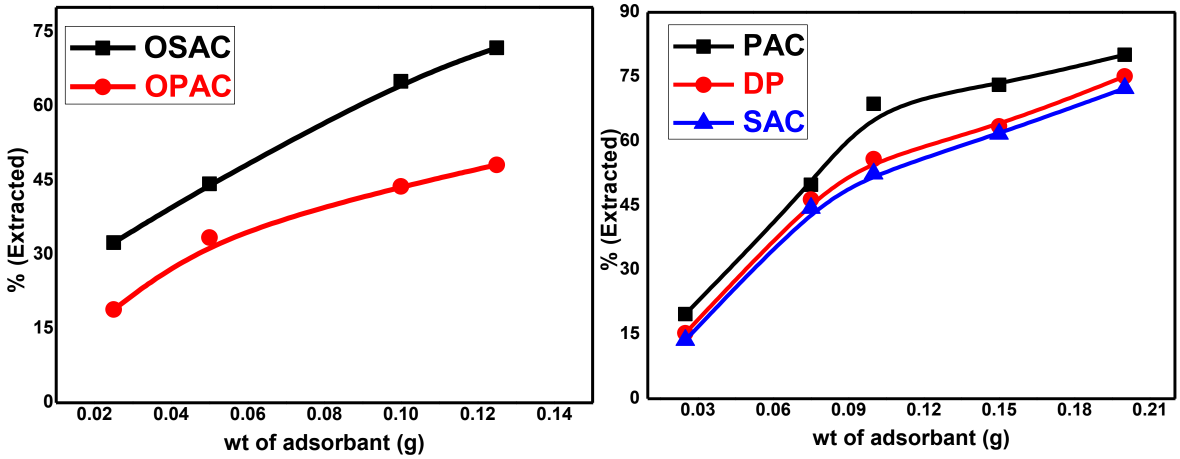

Fig (7): Dosage effect on the extracted of Cd^{2+} using SAC, PAC, DP, OSAC and OPAC. (Conditions: T=25°C; C_o= 50 ppm (PAC, DP, SAC), 300 ppm (OSAC and OPAC), V=0.025 L; time = 5 h)

3.8. Adsorption isotherms

The interaction between adsorbates and adsorbents could be examined by isotherm studies. It provides a significant parameter that helps create the needed system for adsorption. Langmuir and also Freundlich isotherms with regard to adsorption of Cd^{2+} on to SAC, PAC, OSAC, OPAC and also DP in variable con-cent are shown in Figs (8, 9). Lang is convenient with homogenous adsorption surface with the whole sites of adsorption with equivalent adsorbate empathy, Freundlich explained as:

Freundlich isotherm: $$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

Langmuir isotherm: $$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (4)$$

Where q_e amount adsorbed at equilibrium (mg g^{-1}), Ce equilibrium con-cent of the Cd^{2+} (mg L^{-1}) and constant b is connected with the adsorption energy (L/mg), Q_0 is the capacity of Lang monolayer (mg/g), Kf = almost a meter of the capacity of adsorption, and 1/n is the intensity of adsorption. Tables (2, 3) show Langmuir and Freundlich criteria and the obtained constants. R^2 coefficient of regression obtained from model Langmuir may be higher than Freundlich model, which means that Langmuir isotherm is more suitable for the experiment data. The highest monolayer capacity of adsorption (Q_{max}) of SAC, PAC, DP, OPAC and OSAC at 25 ºC was found to be 15.86, 64.05, 59.03, 86.64 and 111.74 mg/g are similar to the data given to experiment. Furthermore, the vital feature of the Langmuir isotherm can be clarified from a non-dimensional separating constant factor (R_L) supposed by the following equation:

$$R_L = \frac{1}{1+bC_0} \qquad (5)$$

Where b (L/ mg) is constant of Langmuir and Con (mg/L) = concentration in solution stage. RL values designates the shape of the isotherm to be negative (RL more than 1), linear (RL = 1), positive (0 less than RL less than1) or irreversible (RL = 0). The values of RL between 0 and 1 show the positive adsorption. Regarding to Cd^{2+} adsorption onto SAC, PAC, DP, OPAC and OSAC, RL values attained are between 0 and 1**,** thus approving that the process of adsorption is positive.

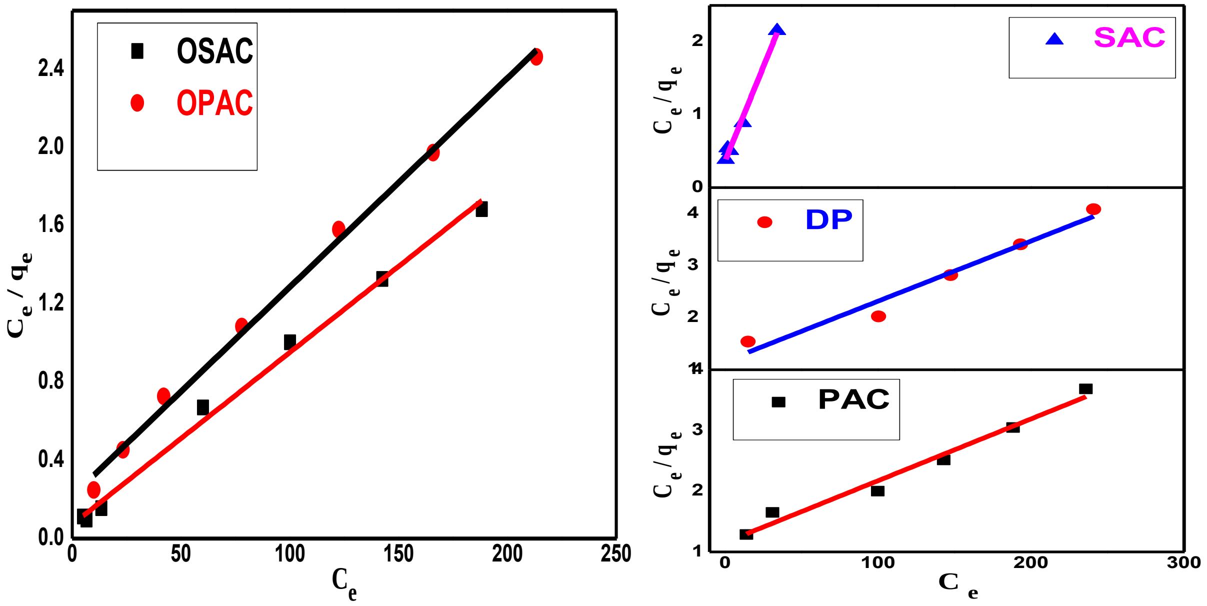

Fig (8): Langmuir against adsorbed of Cadmium using OSAC, OPAC, PAC, DP and SAC.

Table (2): Langmuir for Cd^{2+} using OSAC, OPAC, PAC, DP and SAC.

Adsorbents	Langmuir parameters				
	R^2	Q_{expr} (mg/g)	$Q_{max, fitted}$ (mg/g)	b (mg/L)	R_L
OSAC	0.99	111.74	113.63	0.12	0.02

OPAC	0.99	86.64	93.63	0.04	0.06
PAC	0.97	64.05	100.00	0.008	0.27
DP	0.95	59.03	86.95	0.009	0.25
SAC	0.98	15.86	19.60	0.14	0.12

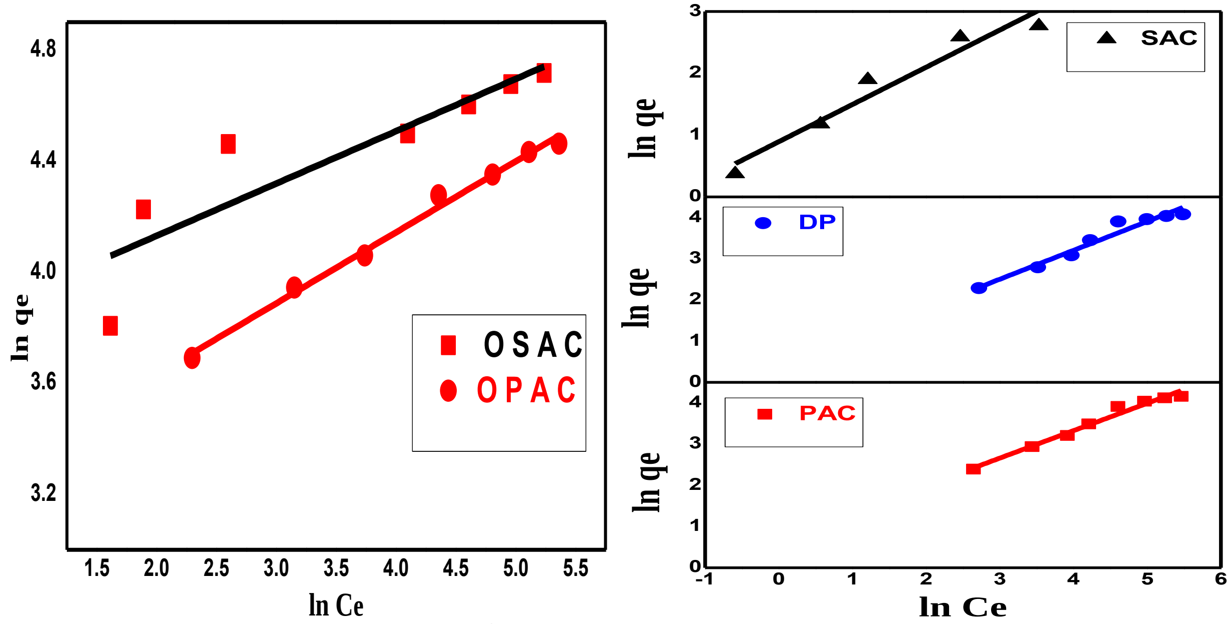

Fig (9): Freundlich plot for adsorption of Cd^{+2} using OSAC, OPAC, PAC, DP and SAC.

Tab (3): Freundlich for Cd^{2+} using OSAC, OPAC, PAC, DP and SAC.

Adsorbents	Freundlich parameters		
	R^2	K_f	l/n
OSAC	0.75	42.69	0.18
OPAC	0.99	22.66	0.25
PAC	0.97	1.94	0.66
DP	0.95	1.49	0.70
SAC	0.92	2.44	0.60

3.9 <u>Kinetics of Adsorption</u>

<u>The pseudo-second order equation and the pseudo-first order equation:</u>

The constant adsorption rate is resolved from the first-order rate expression presented by Lagergren and Svenska. The linear form can be formulated as:

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1\, t}{2.303} \qquad (6)$$

Where q_e and q_t are the adsorbed amounts of cadmium (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the constant adsorption rate of (min^{-1}). Values of k_1 were calculated from the plots of log (q_e- q_t) versus t (min) Fig (10) at concern of 250 ppm (OSAC, OPAC), 150 ppm (PAC, DP) and 50 ppm (SAC) of cadmium. The parallel constant values R^2 are generally low, the experimental q_e values don't match those calculated, attained on the linear and building plots Table (4). This demonstrates cadmium adsorption regarding about OSAC, OPAC, PAC, DP and also SAC is often a non-first-order reaction. The actual second-order kinetic model can be proven down below:

$$\frac{t}{q_t} = \frac{1}{K_2\ q_e^2} + \frac{t}{q_e} \qquad (7)$$

'Where k_2 is the rate of second-order adsorption (g mol^{-1}. min^{-1}). If the second-order kinetics is acceptable, the actual plot of t/qt versus t must indicate some sort of linear relationship. Zero parameter is necessary to possibly be recognized previously and also the potential of sense of balance adsorption, qe is usually made coming from Eq. Additionally, it is very achievable to anticipate the actual conduct in the complete adsorption range. Values of k_2 as well as qe ended up measured in the mountain as well as intercept from the and building plots of t/ qt versus t (minute). The linear and building plots of t/qt versus t (minute) Figure (11) reveals a noticeable contract between both calculated and also experimental q_e values Table (5). The connected constants for the second-order kinetic model highly exceed 0.999 signifying that this kinetic formula is appropriate, the second-order nature of Cd^{2+} adsorption of onto OSAC, OPAC, PAC, DP and SAC adsorbents are also appropriate.

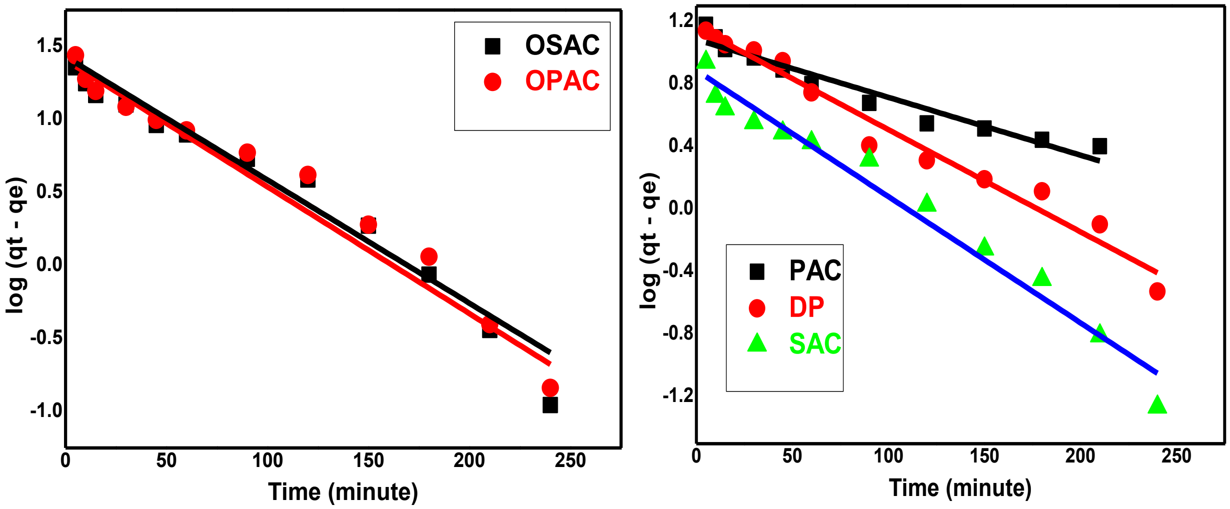

Fig (10): Pseudo of first-order model for the adsorption of Cd^{2+} by SAC, PAC, OSAC, OPAC and DP.

Adsorbent Code	Pseudo - first order			
	q_e exp mg/g	q_e cal mg/g	K_1 (min^{-1})	R^2
OSAC	111.74	25.58	0.01	0.96
OPAC	86.64	26.95	0.01	0.96
PAC	64.05	12.15	8.52	0.93
DP	59.03	14.51	0.01	0.97
SAC	15.86	7.71	0.01	0.96

Tab (4): Kinetic model first - order for using 250 mg/L (OSAC, OPAC), 150 mg/L (PAC, DP) and 50 mg/L (SAC) Cd^{2+}.

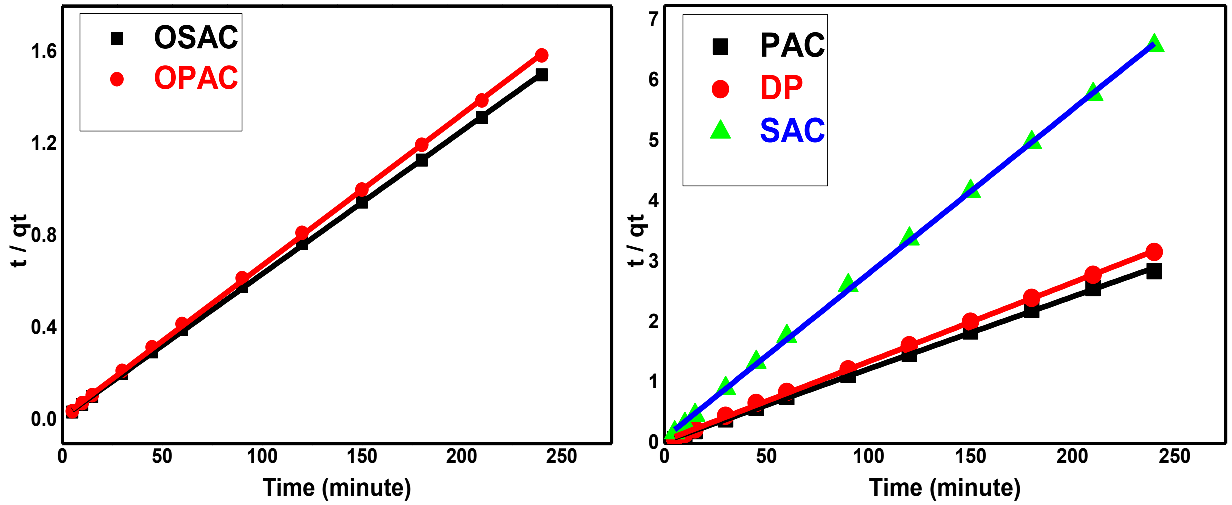

Fig (11): Pseudo of second-order kinetic model for the adsorption of Cd^{2+} by SAC, PAC, OSAC, OPAC and DP.

Tab (5): Kinetic model second - order for using 250 mg/L (OSAC, OPAC), 150 mg/L (PAC, DP) and 50 mg/L (SAC) Cd^{2+}.

Adsorbent Code	Pseudo - second order			
	q_e exp mg/g	q_e cal mg/g	K_2 (g . mol^{-1} .min^{-1})	R^2
OSAC	111.74	161.29	0.21	0.99

OPAC	86.64	153.84	0.18	0.99
PAC	64.05	83.61	0.15	0.99
DP	59.03	76.39	0.13	0.99
SAC	15.86	36.77	0.14	0.99

3.10. Model Intra - particle

Intra-particle using below known as the idea planned by Morris and Weber with equation:

$$q_t = K_d\, t^{0.5} + C \qquad (8)$$

Exactly where C has been the particular intercept along with Kd has been the particular intra- particle rate continual (mg/g min$^{-0.5}$).Accord to model, piece connected with qt versus t$^{0.5}$ need to be linear in case (intra particle) has been involved in the adsorbed process. In the event these traces handed throughout the source, subsequently diffusion of intra-particle has been the particular rate-determining step. At what time these traces wouldn't go through the origin, this was a measure connected with some degree connected with border covering management and this also even more exhibited that the intra-particle hasn't been the one rate restricting step. The values K_d were given within Table (6).

In this particular experiment, the particular plots did not pass through the origin Figure (12), which often indicated the particular intra-particle hasn't been just the particular rate preventing step. Previous studies claimed which multiple phase had been active in the intra-particle diffusion of action. The first part pointed out the particular external surface area adsorption. The second corresponded towards gradual adsorption. The third pointed out the ultimate stability phase the location where the intra-particle diffusion will begin to slow on account of incredibly minimal concentrations of solute in the solution. All interpretation explained that, the particular pseudo-second-order product has been particular best-fit product with the adsorption regarding Cd^{2+} on to OSAC, OPAC, PAC, DP and SAC.

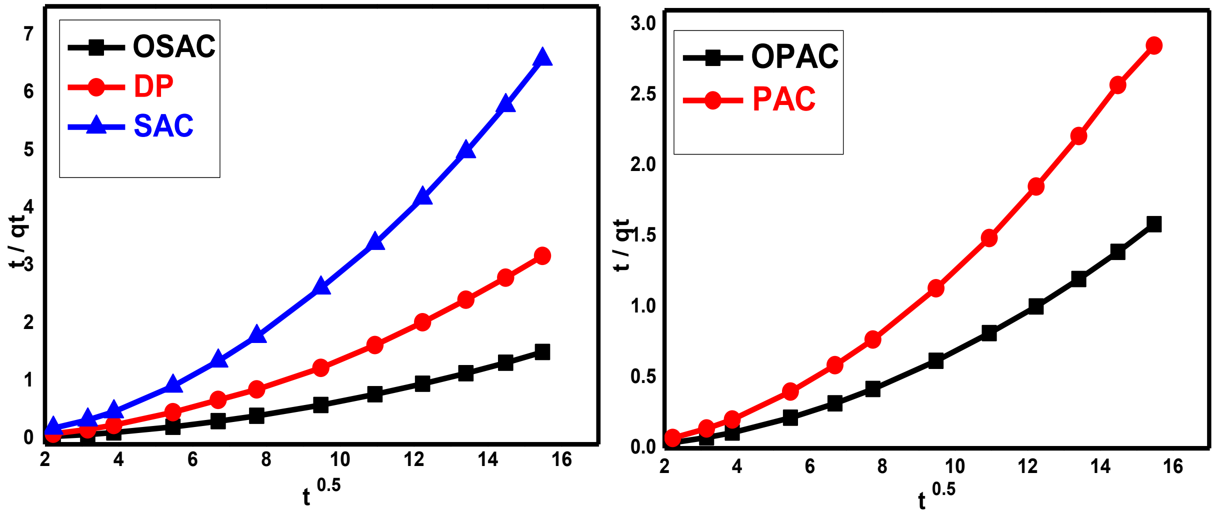

Fig (12): Intra-particle diffusion plots for adsorption of Cd^{+2} on 250 ppm (OSAC, OPAC), 150 ppm (PAC, DP) and 50 ppm (SAC) Cd^{2+}.

Tab (6): parameters Intra-particle for Cd^{2+}using 250 ppm (OSAC, OPAC), 150 ppm (PAC, DP) and 50 ppm (SAC) Cd^{2+}.

Intra-particle diffusion model			
Adsorbent code	R^2	Kd	Intercept
OSAC	0.96	0.10	- 0.35
OPAC	0.96	0.11	- 0.36
PAC	0.96	0.21	- 0.66
DP	0.96	0.23	- 0.72
SAC	0.96	0.48	- 1.51

3.11. Thermodynamic parameters Evaluation

Thermo-dynamic parameter was determined from the variable thermo-dynamic distribute coefficients, k_d with a changeable temperature. The changeable typical free energy, ΔGº, was identified as follows:

$$\Delta G^o = \Delta H^o + T \Delta S^o \qquad (9)$$

The value of ΔH º and ΔS º were calculated from the Van't Hoff equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (10)$$

Plot of In k_d against 1/T obeyed an linear relationship, as shown in Figure (13). ΔS º and ΔH º values were determined from the intercept and slope of linear plot. The thermodynamic parameters are shown in Table (7) the table clearly shows that the values of ΔGº are negative for OSAC, OPAC, PAC, DP and SAC. The negative values involving ΔGº with various conditions stand for this impulsive characteristics of the adsorption process. The values the ΔGº lessen although heat will increase exhibits this increase of impulsive effect and bigger matching probabilities, which leads to the existence of higher relations. Of ΔHº positive value indicates the endothermic behavior of the sorption progression. Positive value of ΔSº shows that the randomness increased through the process of sorption because of the release of molecules of water nearby the ion of metal to the solution.

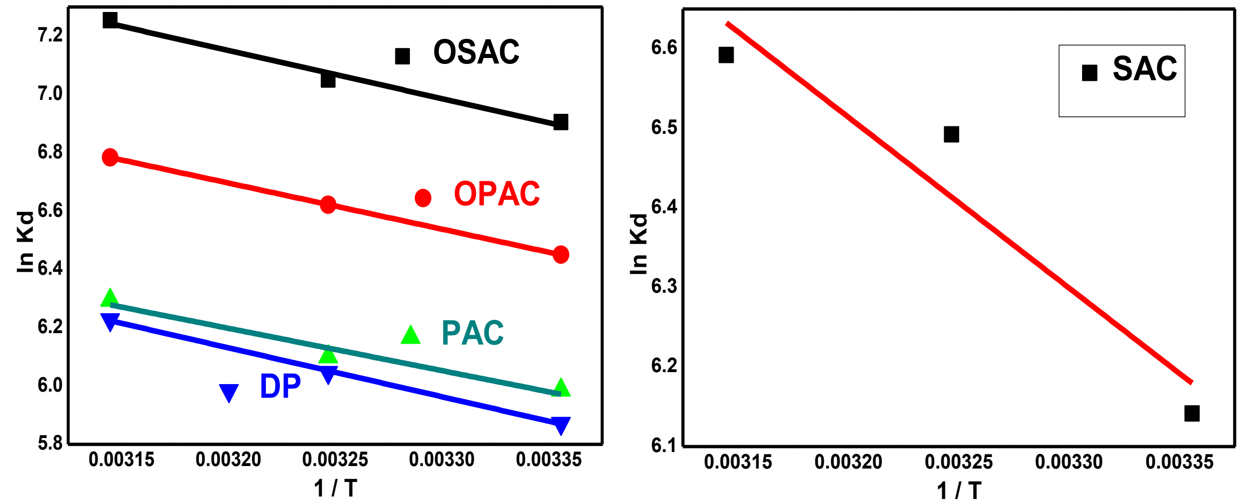

Fig (13): ln Kd against 1/T for parameters thermodynamic of Cd^{2+}. Condition :(C_o = 200 ppm (OSAC, OPAC, PAC and DP) and 50 ppm (SAC), T= 25 - 45 ºC, t = 5h, dose = 25 mg/0.025 L).

Table (7): parameters thermodynamic for Cd^{2+} using OSAC, OPAC, PAC, DP and SAC.

Adsorbents	Cadmium Con-cent (mg L^{-1})	ΔHº (KJ/mole)	ΔSº (KJ/mole)	ΔGº (KJ/mole)		
				298K	308K	318K
OSAC	200	13.76	0.10	-17.06	-18.09	-19.13
OPAC	200	13.15	0.09	-15.98	-16.95	-17.93
PAC	200	12.07	0.09	-14.79	-15.69	-16.59
DP	200	13.96	0.09	-14.54	-15.49	-16.45
SAC	50	17.84	0.11	-15.31	-16.42	-17.53

6. *Conclusion*

There was an efficiency shown for the adsorbents used for removing of Cd (II) from aqueous solutions in the dried papyrus plant and activated carbon. It was indicated by the results that, pH solution values, time of contact, temperature, the dosage of adsorbent, and the initial concentration clearly had an impact on the amount of adsorption of Cd (II). The process of sorption is dependent on pH and the max adsorption was achieved at pH 5. Examinations and study that were performed by variable concentrations of Cd^{2+}. The amount of Cd^{2+} was found to be increasing with the increase of Cd^{2+} concentration within the study area. The kinetic explanations of cadmium OSAC, OPAC, PAC, DP and SAC were carried out according to (first-order), (second-order) and the (intra-particle) dispersal rate mechanism. It was found, by the data, that adsorption kinetics of Cd^{2+}on every adsorbent following the particular model second order on diverse Cd^{2+} con-cent. Just about every isotherm's equilibrium data ended up reviewed using the Langmuir along with Freundlich isotherms, likewise the particular attribute parameters ended up fixed. A result of the results, it can be apparent which the experimental data received a great relationship using the Langmuir isotherm model. Thermodynamic scientific tests confirmed which the strategy of adsorption seemed to be endothermic.

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