Correlation of Activated Carbonized Avocado Pear Seeds (*Persea Americana*) and Activated Carbonized Orange Peels (*Citrus Sinensis*) Adsorptive Potency in Eliminating Cd²⁺ Ions in contaminated water

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Abstract

Water contamination is a very serious problem due to the role and usefulness of water to life. The carbonized orange peels (COP) and carbonized Avocado Pear seeds (CAPS) were impregnated with Potassium hydroxide (KOH) at 1:1 ratio for 48 hours. The KOH impregnated CAPS and COP were washed, air-dried and separately oven dried at 105°C for 6 hours in a muffle furnace (Carbolite AAF1100) at 250°C for 1 hour. The activated carbonized avocado pear seeds (ACAPS) and activated carbonized orange peels (ACOP) were physicochemically characterized using scanning electron microscope (SEM) and Fourier-transform infrared (FTIR) spectrophotometer. Cd^{2+} ions adsorption technique on ACAPS and ACOP was examined by means of the batch adsorption isotherm experimentations and their adsorption model was appraised by means of isotherm models of Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Flory-Huggin. The SEM imageries, showed that ACAPS posessed a large number of varied size pores whereas the ACOP had fewer smaller size pores. The R² values which varied from 0.86 to 1.00 point to the fact that all the isotherm models were capable to clarify the correlation in the obtained data. ACAPS had more adsorption site, however, ACOP took up more Cd^{2+} ion per adsorption site on comparing Flory-huggins isotherm model n_{FH} values vis-a-vis Langmuir isotherm model q_m values. Generally, ACAPS was a superior adsorbent likened to ACOP, it was more than twice as effective for deletion of Cd²⁺ ions in contaminated water owing to a blend of considerable amount of various size openings and surface functional groups with q_m values of 12.35 and 5.67mg/g in that order.

Keywords: Avocado, Orange, Physiosorption, Physicochemical Adsorption, Isotherm.

INTRODUCTION

Water contamination, is a very serious problem due to its role and usefulness to life. Plants and animals cannot survive in water bodies loaded with toxic chemicals, an indication that moderately pure water is a necessity. Increase in bioaccumulation of heavy metals in biological systems over time is owing to heavy metals availability in waters (Nwankwo and Mogbo, 2014).

Cadmium ions (Cd²⁺) occurs in the environment due to natural and anthropogenic activities. Cd²⁺ is very much poisonous to humans, plants and animals. Detrimental effects of Cd²⁺ in humans consist of a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and testicular atrophy etc. The most severe form of Cd²⁺ poisonousness in humans is "Itai-itai", a disease characterized by terrible pain in the bone (Lakherwal, 2014; Singh and Gupta, 2016 and Abdel-Raouf and Abdul-Raheim, 2017).

Methods intended to favor of removal of heavy metal ion from aqueous solutions includes among other: coagulation, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection and chemical precipitation (Hossain *et al.*, 2012; Kumar *et al.*, 2014). Newer methods are ultra-filtration, nano-filtration, and reverse osmosis, however, they are linked with high funds as well as functioning costs (Miretzky *et al.*, 2006). Because of its suitability, easy procedure and easiness of design, adsorption route, is deemed a superior option likened to other methods (Amit and Monocha, 2006). This research is designed to correlate the adsorptive effectiveness of activated carbonized avocado pear seeds (*Persea Americana*)-ACAPS as well as activated carbonized orange peels (*Citrus Sinensis*)-ACOP to get rid of Cd²⁺ ions in contaminated water.

MATERIALS AND METHOD

Sample Collection

Fresh orange and avocado pear was procured from New-Benin market in Benin City Edo State, Nigeria. The orange epicarp as well as avocado seed obtained from the fruit as waste was sliced into bits and rinsed meticulously utilizing distilled water to get rid of filths and dried in an oven at 105°C in an oven for 6 hours. It was filled in a polyethylene bag and knotted.

Activated carbonized avocado pear seeds (ACAPS) and activated carbonized orange peels (ACOP) preparation

The dried avocado pear seeds as well as orange peels was individually pulverized and sieved using BSS-53µm mesh sieve, thereafter they were independently carbonized in muffle furnace (Carbolite AAF1100) at 300°C for 40 minutes. In order to increase the surface area and porosity of carbon obtained, the carbonized avocado pear seeds and orange peels were independently impregnated with Potassium hydroxide (KOH) at 1:1 ratio for 48 hours until the mixture turned into a paste in their containers. KOH was a preferred activating agent because it is a strong dehydrating agent and it modifies the carbon to form porous structure. The activated carbonized avocado pear seeds and orange peels were washed independently with distilled water up until the pH of the filtrate was 7. The ACAPS as well as ACOP were dried inside an oven at 105°C for 6 hours and reheated in a muffle furnace (Carbolite AAF1100) at 250°C for 1 hour.

Preparation and Characterization of Adsorbates

The aqueous solution of Cd²⁺ ions was prepared using analytical grade of cadmium nitrate salt obtained from BDH chemical limited, England and atomic absorption spectrophotometer (AAS) VGP 210 model-Buck Scientific Equipment Inc., in the analytical laboratory of Chemistry Department, University of Benin, Benin City, Nigeria, was utilized to confirm Cd²⁺ ions actual concentrations.

Physicochemical Characterization of Activated Carbonized Avocado Pear Seeds (ACAPS) and Activated Carbonized Orange Peels (ACOP)

Scanning electron microscope (SEM) and Fourier-transform infrared (FTIR) spectrophotometer were utilized to physicochemically typify the activated carbonized avocado pear seeds (ACAPS) as well as activated carbonized orange peels (ACOP) so as to predict the morphology and functional groups or ions present on the materials respectively.

Adsorption Isotherm Studies

Adsorbent dose, pH, time and initial concentrations effect on Cd^{2+} ions elimination was examined. The adsorptive route of Cd^{2+} ions on top of ACAPS as well as ACOP was examined by means of the batch adsorption isotherm experimentations. Batch adsorption experiment was carried out by changing the range of adsorbent dose beginning with 0.2g to 2.5g, contact time starting with 20 minutes to 100 minutes and pH commencing with 3 to 7 at Cd^{2+} ions constant concentration. Initial concentrations of Cd^{2+} ion range was changed beginning with 20.0 to 100.0 mg/L, at optimal adsorbent dose, pH, interaction time as well as 300 rpm stir pace. The equilibrium concentration of Cd^{2+} ions in the samples individually dealt with ACAPS and ACOP was resolved using AAS (Buck scientific model VGP-210).

Mechanism and Isotherm of Adsorption

Classically, adsorption mechanisms include adsorbate diffusion onto adsorbent surface by intermolecular forces in the middle of adsorbate and the adsorbent superficial; adsorbate migrating into adsorbent openings and adsorbate one-tracklayer accumulation on the adsorbent (Iakovleva and Sillanpää, 2013). Nevertheless, the prime means for heavy metal ions (M²⁺) removal, could be ion exchange, owing to existence functional groups diversities atop adsorbents superficial for instance hydroxyl, carboxylic, carbonyl e.t.c, (He *et al.*, 2019). The equilibrium quantities of adsorbate adsorbed as well as adsorption effectiveness of the adsorbent were estimated using equation 1 and 2 in that order:

$$q_e = \frac{(C_0 - C_e)v}{M} \tag{1}$$

$$\%E = \frac{C_0 - C_e}{C_0} \times 100$$
 (2)

The parameters C_0 is the adsorbate's initial concentration (mg/L); q_e and C_e are the Cd²⁺ ions quantity adsorbed (mg/g) as well as adsorbate equilibrium concentration (mg/L), in that order; M is adsorbent weight (g) and v is aqueous solution amount in litres.

Isotherm models of Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Flory-Huggin were utilized to appraise data obtained in this study.

Langmuir isotherm model is based on detail that one-tracklayer adsorption exist, happening homogeneously on the adsorbent operational locations and absence of exchanges amid the adsorbates. It is mainly regularly utilized to evaluate the adsorbate quantity atop an adsorbent as a function of concentration in a specified temperature (Almalike, 2017; He *et al.*, 2019). The Langmuir isotherm equation is shown in equation 3:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m c_e}$$
(3)
(Ghasemi *et al.*, 2018, Lim *et al.*, 2019)

 q_m is the speculative all-out one-tracklayer adsorption capacity (mg/g), and K_L (Lg⁻¹) denotes the Langmuir isotherm constant for adsorption energy.

Freundlich Isotherm model is worthwhile for non-ideal and multilayer adsorption route atop heterogeneous surfaces with a non-uniform allocation of the adsorption heat on top of the surfaces (Iakovleva and Sillanpää, 2013; Lasheen et al., 2017). The Freundlich isotherm equation is shown in equation 4: $\log q_e = \log k_F + (1/n_F) \log C_e$

(Bankole et al., 2019, Lim et al., 2019)

(4)

(5b)

The K_F and n_F remain the constants of Freundlich isotherm for adsorption capacity and strength, in that order. $1/n_F$ is a dimensionless heterogeneousness factor; it's worth, point to which of the adsorption route is spontaneous. When n_F value is greater than 1, spontaneous adsorption conditions apply. The lesser the value of $1/n_{\rm F}$, the more the heterogeneousness (Yildiz, 2017).

Dubinin-Radushkevich is a semi-empirical equation predicated upon micro-pores volume fill-up principle (MVFP) (Worch, 2012), its adsorption mechanism focus on a mechanism of pore filling (Sarı and Tuzen, 2009), it gives consideration into adsorbent porousness as well as adsorption apparent free energy that offer facts on chemisorption or physisorption mechanism, occurring on either homogeneous and heterogeneous surfaces (Essomba et al., 2014; Invinbor et al., 2015; Onwu and Ngele, 2015). Isotherm model of Dubinin-Radushkevich is unfounded on ideal assumptions for instance, steric encumbrance nonexistence in the middle of adsorbed and entering particles, equal efficacy of the adsorption locations and surface uniformity on microscopic level as in Langmuir isotherm (Sarı and Tuzen, 2009; Amin et al., 2015; Moftakhar et al., 2016). The Dubinin–Radushkevich equation (equation 5) has been broadly applied to expound energetic heterogeneousness of solid at low level coverage as onetracklaver zones in micropores (Hossain et al., 2016; Invinbor et al., 2016). Dubinin-Radushkevich isotherm is regularly applied to illustrate solo solute systems adsorption isotherms (Essomba et al., 2014). $\ln q_e = \ln q_D - \beta \cdot \epsilon^2$ (5)

 $[\varepsilon = RTln(1+1/C_e)]$ (5a)

 $E = 1/(-2\beta)^{1/2}$ (Adekola et al., 2016, Ghasemi et al., 2018)

 q_D (mol/g) signifies all-out adsorption capacity, β is the constant of Dubinin–Radushkevich isotherm (mol²/kJ²), it denotes adsorbate free energy per mole as the aforementioned rove to the surface of the adsorbent from inestimable distance. E is adsorption mean free energy (kJ/mol), if E is less than 8, the adsorption means is governed by physisorption route, whilst if E is greater than or equal to 8 or E is less than or equal to 16, then adsorption route is governed via chemisorption (ion-exchange route) route and if E is greater than 16, the adsorption means is governed via diffusion of particle. Gas constant, R = 8.314 J/mol K, absolute temperature represented as T in Kelvin and ε is Polanyi (adsorption) potential energy.

The Temkin isotherm model was based on chemisorptions notion as well as adopts that the adsorption heat of adsorbate molecules reduces linearly by means of adsorbent layer coverage owing to adsorbent-adsorbate exchanges, it similarly adopts a uniform binding energies allocation (Tie et al., 2017). The Temkin isotherm equation is shown in equation 6: $q_e = Bln K_T + Bln C_e$ (6)

 $B = (RT/b_T)$ (Tie *et al.*, 2017)

(6a)

(7b)

B is heat of adsoption (B = RT/b_T); b_T (J/mol), is the Temkin isotherm constant; K_T (L/g), is equilibrium binding constant as well as linked to all-out binding energy (Tie *et al.*, 2017, Ghasemi *et al.*, 2018, Bankole *et al.*, 2019).

Flory-Huggins isotherm is useful in describing the degree of surface coverage appearances of the adsorbate on the adsorbent, This isotherm model can express the feasibility and spontaneity of an adsorption route (Almalike, 2017, Ayawei *et al.*, 2017). The Flory-Huggins isotherm equation is shown in equation 7:

 $Log (\theta/C_o) = Log K_{FH} + n_{FH} Log (1-\theta) (Flory-Huggins isotherm)$ (7)

 $[\theta = (1 - [C_e/C_0])]$ (7a)

 $\Delta G^{\circ} = -RTlnk_{FH}$ (Almalike, 2017, Ayawei *et al.*, 2017)

 θ is the surface coverage of the adsorbent by the adsorbate, C_o is initial concentrations, K_{FH} and n_{FH} are Flory-Huggins model equilibrium constant and number of adsorbate dwelling in adsorption site respectively. ΔG^{o} is standard free energy change. If the ΔG^{o} calculated is negative, it implies adsorption route was spontaneous in nature as well as supports an exothermic nature and vice versa if positive (Almalike, 2017).

On the whole, the isotherm factors are principally calculated from their linear plots intercept and slope. Isotherm models fitting were evaluated using R² values.

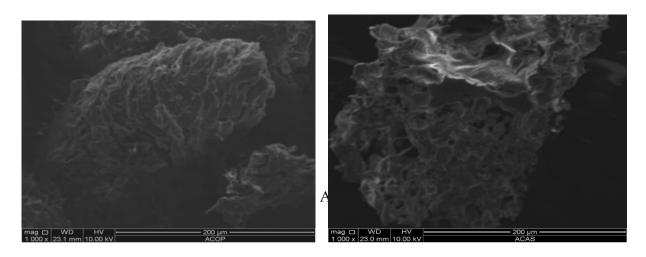
RESULTS AND DISCUSSION

Physicochemical characterization for Activated Carbonized Avocado Pear Seeds (ACAPS) and Activated Carbonized orange peels (ACOP)

Physicochemical characterization of ACAPS and ACOP by means of scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR) are presented below.

Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscope imageries obtained in Fig. 1, revealed surface framework of ACAPS and ACOP.



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The textural structure of ACAPS and ACOP is presented as scanning electron micrograph at x 1000 magnification (Fig.1). The SEM photograph shows that ACAPS, Fig. 1 (b) possesses numerous pores with fibrous structure whereas ACOP, Fig. 1 (a) had less pores of smaller sizes. The SEM images of both adsorbent revealed that they are made up of openings having uneven contours. The fragmention of the particles as well as the disparity in opening proportions gives a picture of the dissimilarities in physical features concerning ACOP as well as ACAPS.

Analysis of Fourier Transformed Infrared Spectroscopy (FTIR)

FTIR analysis spectrums in fig. 2 depict the functional groups existing atop ACAPS as well as ACOP.

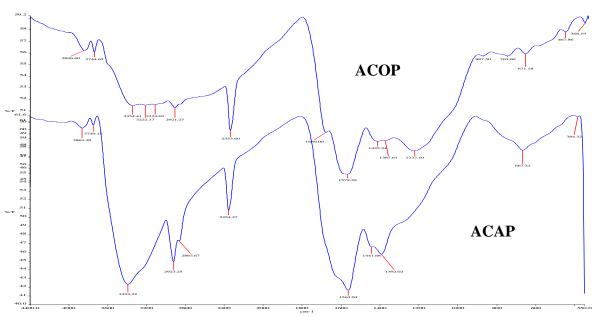


Figure 2: FT-IR Spectrum for ACOP and ACAPS

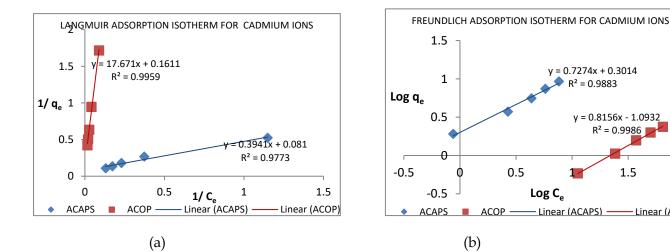
The FT-IR spectrum in lieu of ACAPS disclosed the appearances of an intense band at 3393.15cm⁻¹, denotes medium appearance of NH-stretching vibrations of primary and secondary amine (RNH₂ and R₂NH) group. The peak at 2923.25cm⁻¹ agreed in the direction of OH-stretch of carboxylic acid (-COOH) group. Peak at 1580.61 agreed in the direction of a medium appearance of strong –C-H stretch of alkyl group of -CH₃ (an electron donating moiety with positive inductive effect) that can boost the adsorption of Cd²⁺ (Kingsbury, 2019). Also, peak at 1441.68cm⁻¹ agreed in the direction of a strong C-H bend allocated to alkyl group. ACOP spectrum uncovered characteristic peak at 3354.41 as well as 3124.01 agreeing in the direction of medium N-H stretch of primary and secondary amine groups as well as O-H stretch (H-bonded) linked to carboxylic acid (-COOH) in that order. The peak on 2921.27 and 1425.34cm⁻³ corresponded to a medium appearance of strong –C-H stretch and –C-H bend respectively of alkyl group of -CH₃. The peak at 1689.00 gave a very strong C=O stretch for amides (RCONH₂). A peak at 1237.10cm⁻³ revealed a strong –C-O stretch corresponded to acid, anhydrides and esters (-COOH, R(COOH)₂) and RCOOR.

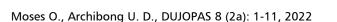
Correlation of Activated Carbonized Avocado Pear Seeds (Persea Americana) and Activated Carbonized Orange Peels (Citrus Sinensis) Adsorptive Potency in Eliminating Cd2+ Ions in contaminated water

Isotherm Models and Parameters Determination for Cadmium Ions Adsorption

The isotherm models aimed at understanding Cd²⁺ ions adsorption on ACAPS as well as ACOP is presented in Fig. 3 and the isotherm factors values as evaluated from the isotherm models are presented in Table 1.

The R^2 worth varies from 0.86 to 1.00 (Figure 3a-e), a signal that the all-inclusive isotherm models utilized, were competent to convey the correlation in figures obtained (Table 1). The Langmuir and Freundlich isotherm constants presented that ACAPS had a stronger affinity for Cd²⁺ ions due to its possession of higher adsorption capacity, adsorption intensity and adsorption energy than ACOP based on their k_F , n_F and k_L (Table 1). These observations are attributed to the various functional groups on the adsorption location of the adsorbents (Fig. 2). ACAPS adsorb higher Cd²⁺ ions likened to ACOP adjudging from the worth of their allout adsorption capacity (q_m) from Langmuir isotherm model (Table 1), is attributed to blend of functional groups as well as significant openings of different dimensions ACAPS possessed (Figure 1). On comparing with other adsorbent, the adsorption capacity of the ACAPS and ACOP was more efficient than bamboo-based activated charcoal and less efficient than that of African wild mango and okro leaves (Table 2). The Freundlich isotherm model revealed that ACOP and ACAPS adsorbents adsorbed the Cd²⁺ ions spontaneously because the two adsorbent had an n_F worth higher than 1, likewise, their ΔG° values from the Flory-Huggins model also confirmed that adsorption route was spontaneous as well as exothermic (ΔG° values were negative, Table 1). The adsorption free energy of Dubinin-Radushkeviek isotherm model (E, kJmol⁻¹) showed that adsorption means is controlled by physiosorption route (E <8, Table 1). The energy per mole (β) required by Cd²⁺ ions to migrate to ACOP surface is higher than for ACAPS surface (Table 1), this is in agreement with the adsorption intensity n_F of Cd²⁺ ions onto ACOP. The isotherm model of Tempkin adsorption showed that the ACAPS has a greater adsorption heat (B) and all-out binding energy (k_T) (Table 1) confirming that ACAPS had firmer hold on the Cd²⁺ ions. The n_{FH} values for ACAPS and ACOP of 2.57 and 14.45 revealed that the ACAP had more adsorption site, however, ACOP took up more Cd²⁺ ion per adsorption site on comparing Flory-huggins isotherm model n_{FH} values vis-a-vis Langmuir isotherm model q_m values.





= 0.7274x + 0.3014

= 0.8156x - 1.0932 $R^2 = 0.9986$

1.5

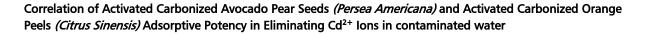
2

Linear (ACOP)

 $R^2 = 0.9883$

Log C

- Linear (ACAPS) –



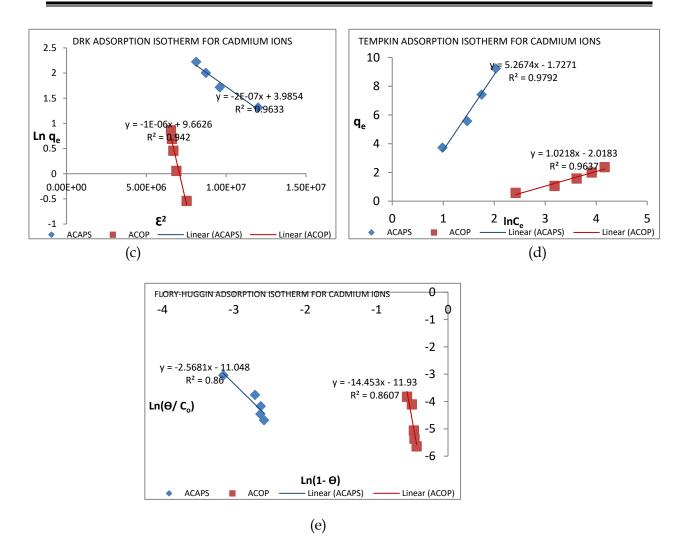


Fig 3: isothermal models graphical illustration for Cadmium ions adsorption

Table 1: Parameters of Adsorption Isotherm Models

Adsorption Isotherm Model	Parameters	Units	ACOP	ACAPS
Langmuir	R ²	-	1.00	0.98
$1/q_{\rm e} = 1/q_{\rm m} + 1/K_{\rm L}q_{\rm m}C_{\rm e}$	k_L	Lg-1	0.0091	0.206
	q _m	mg/g	5.67	12.35
Freundlich	\tilde{R}^2	-	1.00	0.99
$\log q_e = \log k_f + (1/n_f) \log C_e$	K _F	-	0.081	2.00
	$n_{\rm F}$	-	1.23	1.37
Dubinin-Radushkevick (DRK)	R ²	-	0.94	0.96
$\ln q_e = \ln q_m - \beta \epsilon^2$	$q_{\rm D}$	mg/g	15718.60	53.81
$[\varepsilon = RTln(1+1/C_e)]$	β	J/molecule	2x10-7	1x10-6
	E	kJ/mol	0.71	1.58
Tempkin	R ²	-	0.96	0.98
$q_e = Bln K_T + Bln C_e$	K _T	L/g	0.14	0.72
$B = (RT/b_T)$	b _T	J/mol	1431.93	781.56
	В	-	1.02	5.27
Flory-Huggin				
$\log (\theta/C_0) = \log K_{FH} + n_{FH} \log (1-\theta)$	R ²	-	0.86	0.86
$[\theta = (1 - [C_e/C_0])]$	$n_{ m FH}$	-	14.45	2.57
$\Delta G^{\circ} = -RTlnk_{FH}$	$K_{\rm FH}$	$Lmol^{-1}$	1.17x10-12	8.95 x 10 ⁻¹²
	ΔG^{o}	kJ	-69.21	-64.09

Adsorbent	Adsorption Capacity (mg/g)	Reference
ACAPS	12.35	This study
ACOP	5.67	This study
Bamboo-Based Activated Charcoal	4.59	Odoemelam et al., 2015
(BBAC)		
African Wild Mango (Irvingia	21.28	Adekola et al., 2016
Gabonensis) Shell		
okra leaves (Abelmoschus esculentus)	18.80	Khaskheli <i>et al.,</i> 2017

Table 2: Comparison of the Adsorption capacity of ACAPS and ACOP with previous studies

CONCLUSION

The adsorption of Cd^{2+} ions onto ACOP and ACAPS was spontaneous, exothermic and occurred through a physiosorption mechanism as confirmed by ΔG° values from the Flory-Huggins model and n_F values from Freundlich isotherm. ACAPS had a firmer hold for Cd^{2+} ions likened to ACOP owing to functional group location on its surface. ACAPS had more adsorption site, however, ACOP took up more Cd^{2+} ion per adsorption site on Comparing Flory-huggins isotherm model n_{FH} values vis-a-vis Langmuir isotherm model q_m values. On the total, ACAPS was a superior adsorbent likened to ACOP, it was more than twice as effective for elimination of Cd^{2+} ions in aqueous solution owing to a blend of huge amount of openings of different dimensions and it surface functional groups.

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