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CORRELATION OF CARBONIZED AVOCADO SEEDS (*Persea americana)* AND CARBONIZED ORANGE PEELS (*Citrus sinensis*) ADSORPTIVE POTENCY IN REMOVING Cd^{2+} IONS IN AQUEOUS SOLUTION

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ABSTRACT

Man cannot survive without water and water contamination has reduced the availability of healthy water to man. The dried Avocado Pear seed and orange peels were ground into powdery form and sieved using standard test sieve with size BSS-53µm mesh sieve. The pulverized avocado pear seed and orange peel were separately carbonized in a muffle furnace at a temperature of 300 °C for 40 minutes. The physicochemical characterization of the carbonized avocado pear seed (CAPS) and carbonized orange peels (COP) was done using scanning electron microscope (SEM) and Fourier-transform infrared (FTIR) spectrophotometer. The adsorption process of Cd^{2+} ions onto CAPS and COP was studied using the batch adsorption isotherm experiments. Langmuir, Freundlich, Tempkin and Flory-Huggins isotherm models were used to evaluate the data obtained. Cadmium ions had a stronger affinity for CAPS than for COP due to the functional groups present, while the COP had higher intensity, adsorption capacity and spontaneously adsorbed Cd^{2+} ions due to the large number of pores of varied sizes it possesses compared to CAPS. The adsorption mechanism is dominated by physiosorption process. Tempkin adsorption isotherm revealed that the COP a higher heat of adsoption (B) and maximum binding energy than CAPS an indication that the COP held the cadmium ions firmer on its surface compared to that of CAPS. The COP is a better adsorbent compared with CAPS for effective removal of Cadmium ions based on its maximum adsorption capacity of 8.84 and 5.67 for COP and CAPS respectively from Langmuir isotherm model.

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

INTRODUCTION

Man cannot survive without water and water contamination has reduced the availability of healthy water to man. Likewise, plants and animals cannot survive if their water is loaded with toxic chemicals, therefore water need to be moderately pure. Due to bioaccumulation of heavy metals compared to the concentration in the environment, they tend to be dangerous (Nwankwo and Mogbo, 2014).

Cadmium occurs naturally in the environment, through the process of erosion and abrasion of rocks and soils, forest fires and volcanic eruptions.

Cadmium is produced as a by-product mainly from mining, smelting and refining of sulphide ores of zinc. Cadmium is highly toxic to humans, plants and animals. Harmful effects of cadmium in humans include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and testicular atrophy etc. The most severe form of Cd toxicity in humans is "Itai-itai", a disease characterized by excruciating pain in the bone (Lakherwal, 2014; Singh and Gupta, 2016 and Abdel-Raouf and Abdul-Raheim, 2017). Therefore, cadmium ions concentration must be brought below permissible limits using efficient treatment technologies.

There are several methods of removing heavy metal ion from aqueous solutions based on physical, chemical and biological mechanisms, Some of them involve coagulation, foam flotation, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection, chemical precipitation and newer technologies based on ultra-filtration, nano-filtration, and reverse osmosis are associated with high capital and operational costs (Vezentsev *et al.*, 2019). Adsorption process is considered better compared to other methods because of its convenience, easy operation and simplicity of design (Shrimant *et al.*, 2015).

Recently, due to the magnitude of the problem of heavy metals pollution coupled with the cost of purchasing or synthesizing activated carbon, research into new, efficient and cheap methods of heavy metal removal has been on the increase. So a search for low-cost adsorbent to be used for removal of heavy metals from waste waters is necessary and achievable. It is therefore necessary to search for an economical, effective and environmentally friendly adsorbent for treatment of contaminated water. This study seeks to correlate adsorptive potency of carbonized avocado seeds (*Persea Americana)* and carbonized orange peels (*Citrus Sinensis*) in removing Cd^{2+} ions in aqueous solution.

MATERIALS AND METHODS

Collection of Samples

The avocado pear and unpeeled orange was obtained from New-Benin Market in Benin City Edo State, Nigeria. The orange peels and avocado seeds were cut into smaller sizes, washed and rinsed thoroughly with distilled water to remove dirt and impurities and sun dried for 3 day. It was packed in a polyethylene sack bag and covered properly.

Preparation of Carbonized Avocado Pear Seed and Carbonized orange peels

The dried Avocado Pear seed to be carbonized was ground into powder form and sieved using standard test sieve with size BSS-53µm mesh sieve, likewise that of the orange peels. The pulverized avocado pear seed and orange peel were separately placed in a clay pot and placed in a muffle furnace and heated at a temperature of 300 ^{0}C for 40 minutes. The carbonized Avocado Pear seed and orange peel was sieved again using BSS-53µm mesh sieve.

Adsorbents Preparation and Characterization

The nitrate salt of Cd^{2+} ions was used to prepare its aqueous solution. The actual concentrations were confirmed with the use of atomic absorption spectrophotometer (AAS).

Physicochemical Characterization of Carbonized Avocado Pear Seed and Carbonized orange peels

The physicochemical characterization of the carbonized avocado pear seed (CAPS) and carbonized orange peels (COP) was done using scanning electron microscope (SEM; phenom pro suite desktop scanning electron microscope) to view the morphology of adsorbent, Fourier-transform infrared (FTIR system, spectrum BX-PerkinElmer, England) spectrophotometer was used in determining functional groups present.

Adsorption Isotherm Studies

The adsorption process of Cd^{2+} ions onto carbonized avocado pear seed (CAPS) and carbonized orange peels (COP) was studied using the batch adsorption isotherm experiments. The effect of adsorbent doses, time, pH and initial concentrations on the removal of Cd^{2+} ions was investigated. The batch adsorption experiments were conducted by varying Adsorbent dosage from 0.2g to 2.5 g, contact time from 20min. to 100min. and pH from 3 to 7 at constant concentration of Cd^{2+} ions. Initial concentrations of Cd^{2+} ion was varied from 20 mg/l to 100 mg/L, at optimum adsorbent doses, contact time, pH and agitation speed of 300 rpm. The equilibrium concentration of the Cd^{2+} ions in the treated samples was determined using atomic absorption spectrophotometer (Buck scientific model VGP-210).

Adsorption mechanism and Isotherm

The diffusion of adsorbate to adsorbent surface by intermolecular forces between adsorbate and adsorbent on the adsorbent surface; migration of adsorbate into pores of adsorbent and monolayer build-up of adsorbate on the adsorbent are the classical adsorption mechanisms (Iakovleva and Sillanpää, 2013). However, the principal mechanism for the removal of heavy metal ions (M^{2+}) may be ion exchange, due to the presence of varieties of functional group on the surfaces of the different adsorbents such as hydroxyl, carbonyl, carboxylic e.t.c, these are the active ion exchange sites which are efficient in capturing heavy metal ions (Khan *et al.*, 2013).

The perception of adsorbent processes on surface, type of adsorbate monolayer or multilayer and adsorbent capacity is simplified by adsorption isotherms (Iakovleva and Sillanpää, 2013). The equilibrium amount of adsorbate adsorbed (or adsorption capacities) and adsorption efficiency from the aqueous solution were calculated using equation 1 and 2 respectively:

$$\mathrm{q_e} = \frac{(\mathrm{C_o} - \mathrm{C_e})\mathrm{v}}{\mathrm{M}} \qquad (1)$$

$$\%\mathrm{E} = \frac{\mathrm{C_o} - C_e}{\mathrm{C_o}} \times 100 \qquad (2)$$

In this research study, Langmuir, Freundlich, Tempkin and Flory-Huggins isotherm models will be used to evaluate the data obtained. Langmuir isotherm model is predicated on the fact that there is monolayer adsorption which occurs uniformly on the active sites of the adsorbent and there are no interactions between the adsorbates. It is most commonly used to quantify the amount of adsorbate on an adsorbent as a function of concentration at a given temperature

(Almalike, 2017; He *et al.*, 2019). The Freundlich Isotherm model is useful for non-ideal sorption as well as a multilayer sorption process on heterogeneous surfaces with a non-uniform distribution of the adsorption heat over the surfaces (Iakovleva and Sillanpää, 2013; Lasheen *et al.*, 2017). However, Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption (Essomba *et al.*, 2014), hence the use of Dubinin–Radushkevich (DRK) isotherm model which is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level (Sarı and Tuzen, 2009; Amin *et al.*, 2015; Moftakhar *et al.*, 2016). DRK is a semi-empirical equation based on the theory of volume filling of micropores (TVFM) (Worch, 2012), whose, adsorption process follows a pore filling mechanism (Sarı and Tuzen, 2009), thus giving an understanding into the adsorbent porosity and apparent free energy of adsorption which provide information on the nature of the adsorption process or sorption mechanism, that is, whether chemisorption or physisorption is occurring on both homogeneous and heterogeneous surfaces (Inyinbora *et al.*, 2015; Onwu and Ngele, 2015). The DRK equation has been widely used to explain energetic heterogeneity of solid at low coverage as monolayer regions in micropores (Hossain *et al.*, 2016; Inyinbor *et al.*, 2016). DRK isotherm is commonly used to describe the sorption isotherms of single solute systems (Essomba *et al.*, 2014). The Temkin isotherm model was developed on the idea of chemisorptions and assumes that the heat of adsorption of the sorbate molecules decreases linearly with adsorbent layer coverage due to adsorbate-adsorbent interactions, it also assumes a homogeneous distribution of binding energies (Tie *et al.*, 2017). Isotherm models fitting were evaluated using R^2 values. The linear equations of the different isotherm model are stated below:

$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m C_e}$ Langmuir isotherm) 1 (Ghasemi *et al.*, 2018,

Lim *et al.*, 2019)

$\log q_e = \log k_f + (1/n_f)\log C_e$ (Freundlich isotherm) 2 (Bankole *et al.*, 2019,

Lim *et al.*, 2019)

$\ln q_e = \ln q_D - \beta.\varepsilon^2$ (Dubinin–Radushkevich isotherm) 3 (Adekola *et al.*, 2016, Ghasemi *et al.*, 2018)

$[\varepsilon = RT\ln(1+1/C_e)]$ 3a

$E = 1/(-2\beta)^{1/}$ 3b

$q_e = B\ln K_T + B\ln C_e$ (Tempkin isotherm) 4 (Tie et al., 2017) $B = (RT/b)$ 4a

The parameters C_0 is the initial concentration of adsorbate (mg/L); q_e and C_e are the quantity of metal ions adsorbed (mg/g) and concentration (mg/L) at equilibrium, respectively; M is the adsorbent mass (g) and V is the volume of the aqueous solution, q_m is the theoretical maximum monolayer sorption capacity (mg/g), and K_L (L/g) represents the Langmuir isotherm constant for adsorption energy.

The K_F and n_F are the Freundlich isotherm constants describing adsorption capacity and intensity, respectively. 1/n is a dimensionless heterogeneity parameter; its value indicates whether the adsorption process is spontaneous. Spontaneous adsorption conditions apply in cases where n values are greater than 1.

The smaller the value of 1/n, the greater the heterogeneity (Yildiz, 2017). q_D (mol/g) denotes maximum adsorption capacity for DRK, β is the DRK isotherm constant (mol^2/kJ^2), it is referred to be the free energy per mole of sorbate as it migrate to the surface of the sorbent from infinite distance.

E is mean free energy of adsorption (kJ/mol), if $E<8$, the adsorption mechanism is dominated by physiosorption process, if $8 \leq E \leq 16$, the adsorption process is dominated by chemosorption (ion-exchange process) process and if $E > 16$, the adsorption mechanism is dominated by particle diffusion.

R is gas constant =8.314 J/mol K, T is absolute temperature expressed in Kelvin and ε is Polanyi (adsorption) potential energy, B is heat of adsoption ($B = RT/b_T$); b_T (J mol $^{-1}$), is the Temkin isotherm constant; K_T, (L g^{-1}), is the equilibrium binding constant and related to the maximum binding energy (Tie *et al.,* 2017, Ghasemi *et al.*, 2018, Bankole *et al.,* 2019). In general, the isotherm parameters are mainly determined from the slope and intercepts of their linear plots.

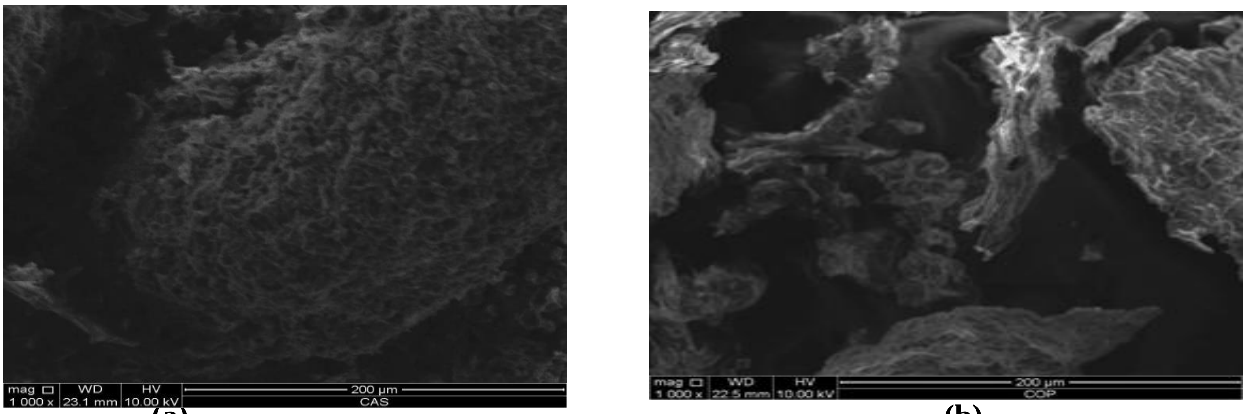
RESULTS

Physicochemical characterization for Carbonized Avocado Pear Seed (CAPS) and Carbonized orange peels (COP)

The carbonized avocado pear seed (CAPS) and carbonized orange peels (COP) were physicochemically characterized using scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR). The following physicochemical characterizations were obtained:

Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscope images taken as shown in Figure 1 shows the surface morphology of the carbonized avocado pear seed (CAPS) and carbonized orange peels (COP)



(a) **(b)**

Figure 1: CAPS (a) and COP (b) SEM images

Fourier Transformed Infrared Spectroscopy (FTIR) analysis

The spectrum of FTIR analysis shown in Figure 2, revealed the functional groups present on carbonized avocado pear seed (CAPS) and carbonized orange peels (COP).m

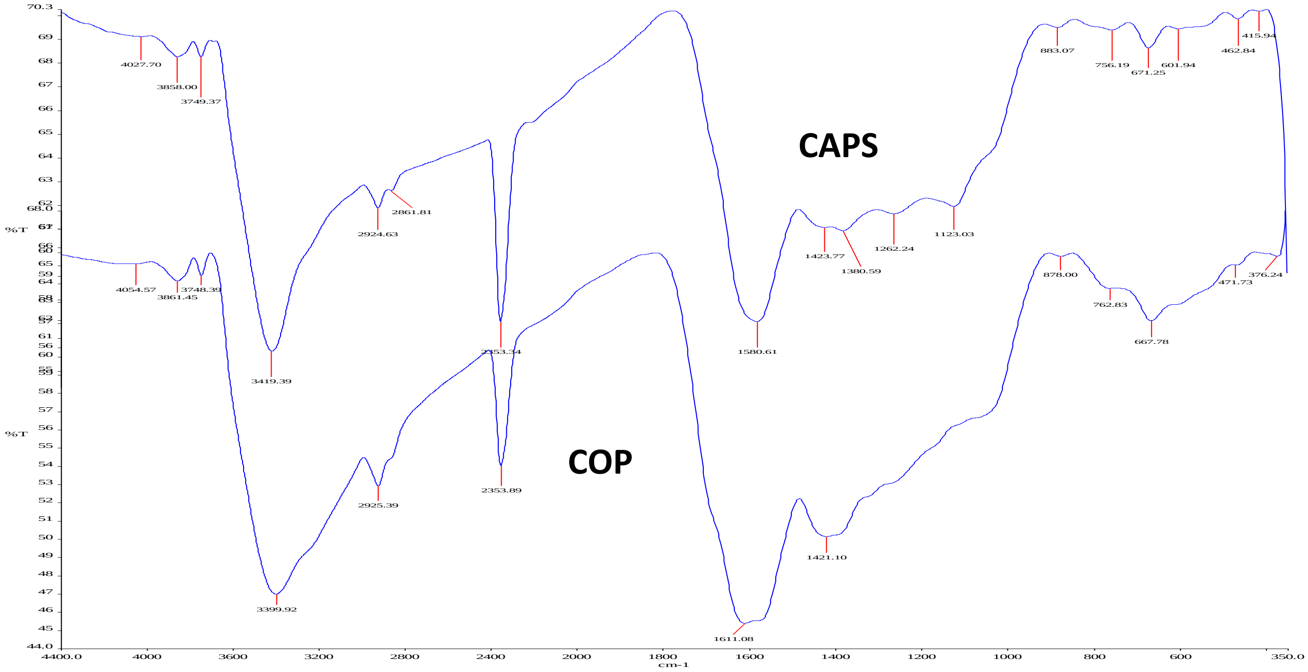
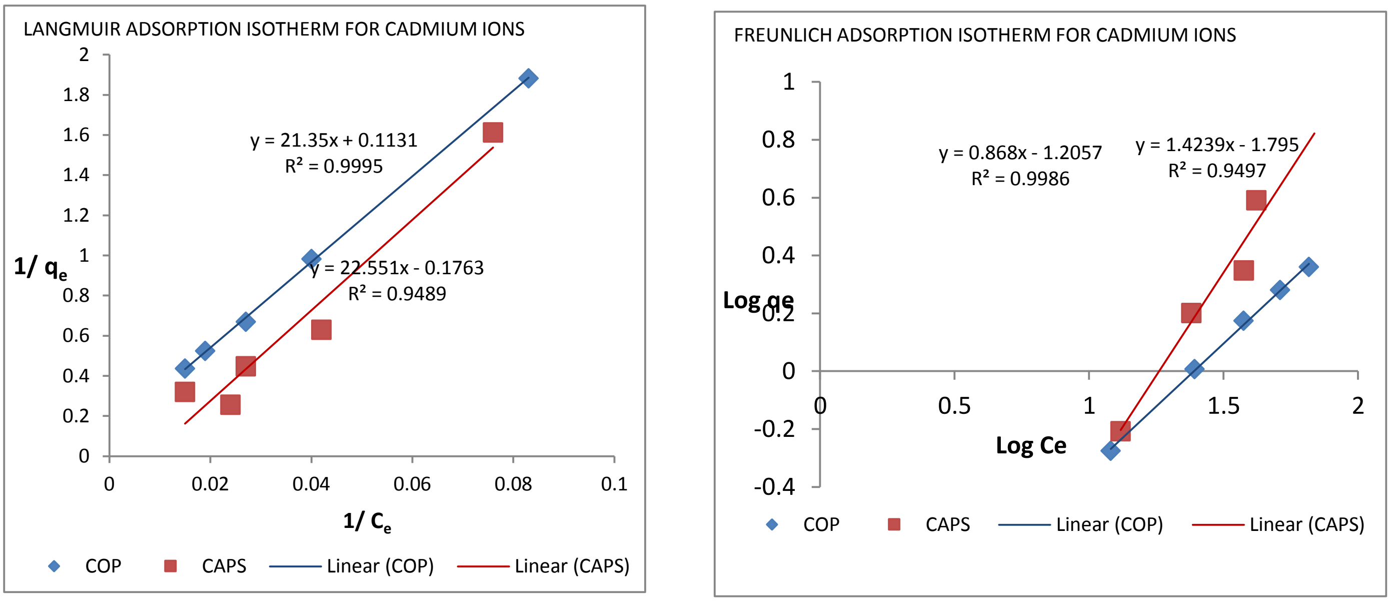
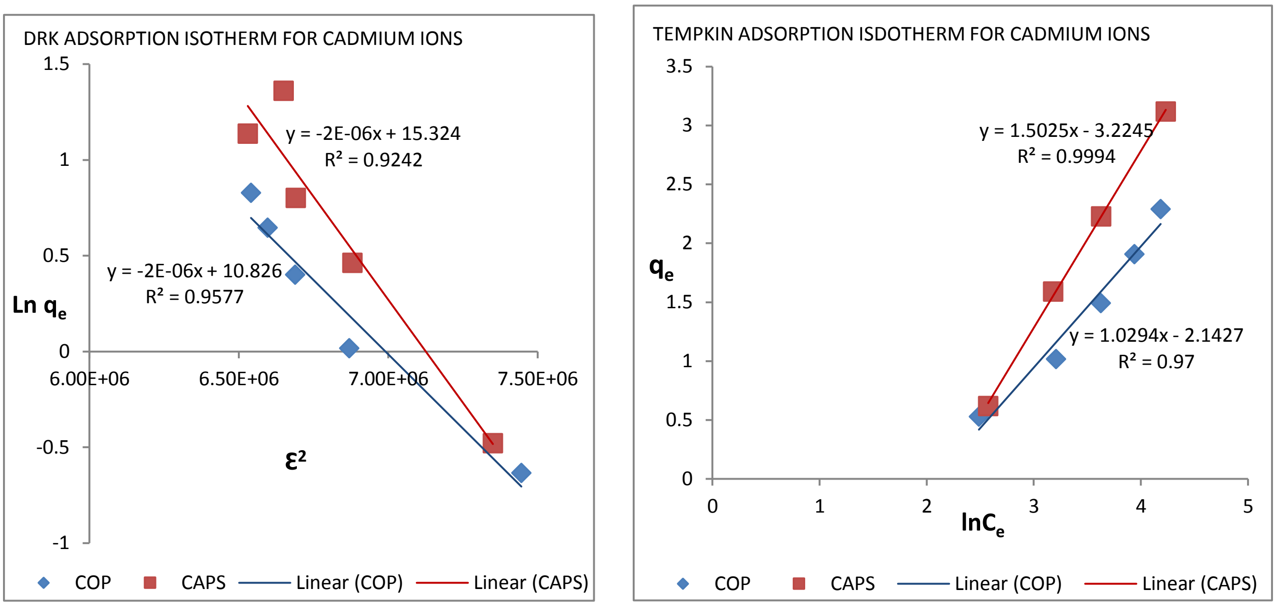


Figure 2: FT-IR Spectrum for CAPS and COP

Isothermal Models for Cadmium Ions Adsorption

The various isothermal models for the adsorption pattern of cadmium on carbonized avocado pear seed (CAPS) and carbonized orange peels (COP) are shown in Figure 3.





(c) (d)

Figure 3: Graphical representation of isothermal models for Cadmium ions adsorption

Adsorption Isotherm Model Parameters Determination

The value of the isotherm parameters as determined from the isotherm models are shown in

Table 1: Adsorption Isotherm Model Parameters

Adsorption Isotherm Model	**Parameters**	**Units**	**CAPS**	**COP**
Langmuir $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m C_e}$	R^2	-	0.95	1.00
	k_L		7.82×10^{-3}	5.30×10^{-3}
	q_m	mg/g	5.67	8.84
Freundlich $\log q_e = \text{loq}k_f + (1/n_f)\log C_e$	R^2	-	0.95	1.00
	K_F	-	0.016	0.062
	n_F	-	0.70	1.15
Dubinin-Radushkevick (DRK) $\ln q_e = \ln q_m - \beta.\varepsilon^2$ $[\varepsilon = RT\ln(1+1/C_e)]$	R^2	-	0.92	0.96
	q_D	mg/g	452×10^6	5.03×10^4
	β	J/molecule	2×10^{-6}	2×10^{-6}
	E	kJ/mol	0.500	500
Tempkin $q_e = B\ln K_T + B\ln C_e$ $B = (RT/b_T)$	R^2	-	1.00	0.97
	K_T	L g^{-1}	0.12	0.13
	b_T	kJ mol^{-1}	1.68	2.45
	B	J mol^{-1}	1.03	1.50

DISCUSSION

Scanning Electron Microscopy (SEM) Analysis

The SEM photograph, revealed that carbonized orange peel posesses a large number of pores of varied sizes while the carbonized avocado pear seed had fewer pores of smaller sizes. The SEM image also show that the particles consist of pores having irregular shapes. The fragmention of the particles and the difference in pore size depicts the differences in physical characteristics between the carbonized orange peel and carbonized avocado pear seed shell.

Fourier Transformed Infrared Spectroscopy (FTIR) analysis

The FT-IR spectrum for carbonized avocado pears seed (CAPS) showed the characteristics of a very strong band at 3419.39 cm^{-1} which represents NH-stretching vibrations of primary amine RNH_2 and secondary amine R_2NH group. Also, a peak at 2924.63 cm^{-1} corresponding to OH-stretch of carboxylic acids (-COOH) group. The peak at 1580.61 cm^{-l} Corresponded to a fairly strong –C=C- stretch of alkene conjugate. A peak at 1262.24 cm^{-1} corresponded to a strong C-O stretch assigned to carboxylic acids (-COOH), ester (-COOR) and acid anhydride (-$RCO)_2O$) groups. At 1123.03 cm^{-1} a strong peak depicting a strong C-O stretch was observed, corresponding to ether (ROR). The presence of mono-substituted and 1, 2-disubstituted benzene was revealed by a strong C-H bend at a peak of 756.19 cm^{-1}. The spectrum of carbonized orange peels (COP) revealed characteristic peak at 3399.92 cm^{-1} and 2925.39 cm^{-1} corresponding to a medium N-H stretch of primary and secondary amines group and O-H stretch of carboxylic acids (-COOH) respectively. A peak at 1611.08 cm^{-1} reveal a medium strong –NH band corresponding to amine and amide (-RNH_2 and $RCONH_2$). A peak at 762.83 cm^{-1} revealed a strong C-H bend corresponding to monosubstituted benzene. The presence of more sites of carboxylic (-COOH), alkene conjugate (–C=C-), mono and disubstituted benzene groups on CAPS increases its heterogeneity (Silverstein *et al.*, 1981).

Adsorption Isotherm Model Parameters

The R^2 value ranges from 0.92 to 1.00, an indication that the entire isotherm models were able to express the relationship in the data obtained (Table 1). The Langmuir isotherm constant revealed that the cadmium ions had a stronger affinity for COP than for CAPS (Table 1). This is attributed to the possession of a large number of pores of varied sizes by COP compared to that of CAPS in their morphology (Figure 1) and the functional groups their adsorption site (Figure 2). The properties COP possessed, supports its ability to adsorb more cadmium ions on its surface compared to CAPS based on the value of their maximum adsorption capacity from Langmuir isotherm model (Table 1). The Freundlich isotherm model revealed that COP had higher intensity and adsorption capacity than CAPS. The

Freundlich isotherm model also asserted that the COP adsorbent adsorbed the Cd^{2+} ions spontaneously. Dubinin-Radushkeviek isotherm model the mean free energy of adsorption (E, kJ/mol) revealed that the adsorption mechanism is dominated by physiosorption process. Tempkin adsorption isotherm revealed that the COP has a higher heat of adsorption (B) and maximum binding energy than CAPS an indication that the COP has a firmer hold on the cadmium ions on its surface compared to that of CAPS.

CONCLUSION

Despite the fact that both adsorbents were able to remove cadmium ion to a certain extent, the carbonized orange peel is a better adsorbent compared with carbonized avocado pear seed for effective removal of Cadmium. The cadmium ions was more spontaneously adsorbed and had a stronger affinity for COP than CAPS and this is an attribute of the functional group site on COP surface and the large number of pores of varied sizes it possessed compared to CAPS. The adsorption mechanism was dominated by physiosorption process. Tempkin adsorption isotherm revealed that the COP has a higher heat of adsorption (B) and maximum binding energy than CAPS an indication that the COP had a firmer hold on the cadmium ions on its surface compared to that of CAPS.

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