

Adsorption of Cadmium(II) Ions from Aqueous Solution onto Activated Carbon Based Cola Nut Shells Wastes.

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ABSTRACT

The aim of this work was to study the adsorption of Cd^{2+} ions from aqueous solution using activated carbons prepared from cola nut shells wastes using zinc chloride and potassium hydroxide as activation agent.

The influence of parameters such as contact time, adsorbent dosage, solution pH, solution initial concentration was studied. Experiments were carried out in a batch system method at room temperature. For both adsorbent, the equilibrium time was reached at 10 min. The maximum adsorption quantities obtained with adsorbent mass of 0.01 g at pH of 6.0 at initial concentration of 240 mg/L were 129.584 mg/L and 157.088 mg/L for activated carbon based $ZnCl_2$ (ACZ) and activated carbon based KOH (ACK) respectively. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models were used to illustrate the experimental data and isotherms constants for both adsorbent. The experimental data fitted well the Freundlich isotherm model. The rates of adsorption obeyed

pseudo-second order model with good correlation for the two adsorbents. The increased concentration of the Cd^{2+} ions in solution lead to decrease in the adsorption quantities. This study shows that ACK is a better adsorbent for the elimination of Cd^{2+} ions from aqueous solution than ACZ.

Key words: Adsorption, Cadmium(II) ions, Cola nut Shells, $ZnCl_2$ and KOH

INTRODUCTION

Heavy metals are pollutants in water and wastewaters, and have become a public health nuisance due to their non-biodegradable and continual nature. The toxicity risk of these metals increases through accumulation in living organisms and following bio amplification in the food chain [1]-[2]. Cadmium is one of the heavy metals widely used in industries such as the electroplating, nickel-cadmium batteries, pigments, plastics, pesticides, dyes, and textile operation [3]. Cadmium compounds are often attached with small particles in air and the ingestion through breathing causes harm to the lungs. The permissible limit for

cadmium in waste water as described by the World Health Organization (WHO) is 0.003 mg/L [4]. Because of the toxicity and non-degradable nature of cadmium, scientists have carried out

significant work on the removal of cadmium from aqueous solutions and industrial effluents. The main techniques used to remove cadmium ions from aqueous streams include ion-exchange chromatography, reverse-osmosis, chemical precipitation and adsorption. Adsorption method has been employed for the elimination of Cd(II) ions due to its benefits such as easiness, rapidness, suitability, and design costs for the equipment and process. The elimination of Cd(II) ions from aqueous solutions has been carried out by using different kinds of adsorbents such as polymer [5] and modified-polymer [6], ion-exchange resin [7], modified carbon nanotubes, Nano-membrane [8] and activated carbon. However, such type of adsorbents is not ecofriendly and cost-effective for practical wastewater treatments. Therefore, great attention has been taken to research for different types of low-cost adsorbent for the removal of Cd(II) ions from aqueous solutions. In this context Essomba *et al.*, 2014 [9] used kaolinite and meta-kaolinite as adsorbent for the elimination of cadmium ions in aqueous solution but as compared to other adsorbents the adsorption quantities were still very low. In this study activated carbon prepared by

zinc chloride (ACZ) and potassium hydroxide (ACK) activation of cola nut shells wastes were used for the removal of Cd(II) ions.

MATERIALS AND METHOD

Preparation of Adsorbent

Cola nut shells were initially washed with deionized water, sun dried, and grained mechanically using a grinding machine (RETSCH) then screened through a sieve (RETSCH) to get geometrical size of ≤ 1.5 mm, which by the use of a beaker was kept into an oven at 110°C for a period of 24 hours, removed, and cooled in a desiccator containing CaCl₂ (drying agent) for 30 min. The lignocellulosic material was removed from the desiccator, and a 1:1 mass reagent ratio was applied, mixed, and dried for 24 hours at 110°C;

Carbonization and activation were accomplished in a single step by carrying out the thermal decomposition of the raw material (cola nut shells) impregnated with ZnCl₂ and KOH as activating agent in the absence of oxygen in a carbolite furnace at 500°C for 1 hour as resident time. After activation, the furnace was allowed to cool to room temperature. Washed several times with distilled water until a neutral pH was

achieved. Later the carbon paste was dried in an oven at 110°C for at least 24 hours

Adsorbents Characterization

The surface functional groups of the prepared activated carbon were estimated by Fourier Transform Infrared (FTIR) spectroscopy (Alpha - Bruker). FTIR spectra of sample were recorded between 400-4000 cm^{-1} . The BET specific area, total pore volume and pore size of ACs were determine by standard multipoint

before application [10].

techniques of nitrogen adsorption using MicrometricsASAP 2020equipment. The iodine number was done to measure micropore content of the AC using the method described by the American Society for Testing and Materials (ASTM D2866-94) [10].

Table1: Physicals properties of activated carbon

	Surface area ($\text{m}^2.\text{g}^{-1}$)	Pore volume ($\text{cm}^3.\text{g}^{-1}$)	Pore size (nm)	Iodine number ($\text{mg}.\text{g}^{-1}$)
Activated carbon-KOH	2.0448	0.0048	9.4203	513.9450
Activated carbon -ZnCl	647.737	0.3321	3.8013656	7072

Preparation of cadmium(II) ionssolution

A stock solution of cadmium(II)ions of concentration (1000 mg/L) were prepared by dissolving 2.329g of $\text{CdSO}_4 \cdot 3\text{H}_2\text{O}$ in a 1000ml volumetric flask. This was swirled until all the salt

Batch Adsorption

Batch adsorption tests were carried out by mechanical agitation at room temperature. For each run, 20 mL of cadmium(II) ions of known initial concentration (40-240mg) weretreated with a known weight of ACZ and ACK after agitation, the solutions were filtered, direct complexometric titration

dissolved,transferred into a 1L volumetric flask and completed with distilled water up to the mark. This solution was stirred on a magnetic stirrer for onehour to obtain homogeneity. All experimental solutions were prepared by diluting the stock solution to the required concentration.

method were then carried out. The pH of the solution was adjusted either with 0,1NHCl or 0,1N NaOH as required. The percentage removal (% R) and quantity adsorbed (Q_t) per unit of mass of cadmium ions were calculated using the following equationsis.

$$\%R = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

$$Q_t = \frac{C_0 - C_t}{m} V \quad (2)$$

Where C_e is the concentration of adsorbate at equilibrium; C_t is the concentration of adsorbate at time t ; C_0 is the initial concentration; m is the mass of the adsorbent; and V is the volume of the adsorbate.

Adsorption isotherm models

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. In order to successfully represent the dynamic adsorptive behaviour of any substance from the fluid to the solid phase, it is important to have a satisfactory description of the equilibrium state between the two phases composing the adsorption system [11]. Classical adsorption models are used to describe the equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution (represented by adsorption isotherms). The Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich (D-K-R) and Tempkin adsorption models were used to analyse the equilibrium data of adsorption of cadmium(II) onto the activated carbon.

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is one of the most common isotherm models for modelling equilibrium data in solid-liquid systems. This model characterized a monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The general form of the Langmuir equation is [12]

$$Q_e = Q_m \frac{K C_e}{1 + K C_e} \quad (3)$$

Where, C_e is the equilibrium concentration (mg.L^{-1}), Q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mg/g), b is the Langmuir adsorption constant (L.mg^{-1}) and Q_m is the maximum amount per unit mass of adsorbent to form a complete monolayer on the surface (mg/g). The linear form of this equation is given below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K} \quad (4)$$

The effect of isotherm shape can be used to predict whether an adsorption system is “favourable” or “unfavourable”. The essential features of the Langmuir isotherm

can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined by the following relationship:

$$R_L = \frac{1}{1+kC_0} \quad (5)$$

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [13].

Freundlich adsorption isotherm

The Freundlich equation is an equation based on adsorption on a heterogeneous surface. Its general form equation is given by equation

$$Q_e = K_F C_e^{1/n} \quad (6)$$

Where, Q_e is the quantity of solute adsorbed at equilibrium, also called the adsorption density (mg.g^{-1}), C_e is the concentration of adsorbate at equilibrium (mg.L^{-1}), K_F and n are empirical constants dependent on several factors. The linear form is given by taking the logarithm on both as:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Dubinin-Kaganer-Radushkevich (D-K-R)

This model envisages the heterogeneity of the surface energies and can be written in the following linear form (8) [13].

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2 \quad (8)$$

Where,

$\varepsilon = RT \ln(1 + \frac{1}{C_e})$ known as Polanyi Potential. The mean sorption energy, E (kJ/mol), which is defined as the free energy transfer of one mole of solute from infinity of the surface of the adsorbent, can be calculated using the calculated value of β , from:

$$E = (2K')^{-1/2} \quad (9)$$

If the magnitude of E is between 8 and 16 kJ.mol^{-1} , the sorption process is supposed to proceed via chemisorption, while for values of $E < 8 \text{ kJ.mol}^{-1}$, the sorption process is of physical nature.

Tempkin adsorption isotherm

Tempkin isotherm assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent - adsorbate interaction [14].

$$Q_e = \frac{RT}{bT} (\ln A_T + \ln C_e) \quad (10)$$

Where b is the Tempkin constant related to heat of sorption (J/mol) and K_T is the Tempkin isotherm constant (L/g).

Kinetics adsorption models

In the present work, the kinetics of adsorption of cadmium ions onto activated carbon was studied using four kinetic models:

Pseudo – first-order kinetic model: the pseudo-first-order equation of Lagergren is generally expressed as follows [12]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (11)$$

Where Q_e and Q_t refer to the amount of pollutant adsorbed (mg.g^{-1}) at equilibrium and at any time, t (min), respectively, and k_1 is the equilibrium constant of pseudo-first-order sorption (min^{-1}). Integration of equation (11) for the boundary conditions; $t = 0$ to t and $Q_t = 0$ and its rearrangement gives:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (12)$$

Pseudo-second-order kinetic model: If the rate of sorption is a second order mechanism, the pseudo-second-order chemisorption kinetic rate is expressed as [9]:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (13)$$

where k_2 is the rate constant of pseudo-second-order sorption ($\text{g.mg}^{-1}.\text{min}^{-1}$). The integrated and rearranged form of equation (13) is:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (14)$$

The initial adsorption rate h ($\text{mg.g}^{-1}.\text{min}^{-1}$), when t tends to 0 is given by:

$$h = k_2 Q_e^2 \quad (15)$$

Elovich kinetic model: The Elovich equation was first developed to describe the kinetics of chemisorptions of gas onto solids [4]. The linear form of the Elovich model is presented by the following equation:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (16)$$

Intraparticle diffusion kinetic model: the transportation of adsorbate from solution phase to the surface of the adsorbent particles may be controlled either by one or more steps such as: (i) film or external diffusion, (ii) pore diffusion, (iii) surface diffusion and (iv) adsorption on the pore surface, or a combination of more than one step [15]. The general equation of intraparticle diffusion model is given by [13]:

$$\ln R = \ln K_{id} + \alpha \ln t \quad (17)$$

where, $\ln R$ is the amount of pollutant adsorbed at time t , ($\text{mg.g}^{-1}.\text{min}^{-1}$) K_{id} is the intraparticle rate constant and α the intercept.

Results and Discussions

Adsorbent characterisation

The FTIR spectrum of activated carbon is shown in (Figs.1 and 2)

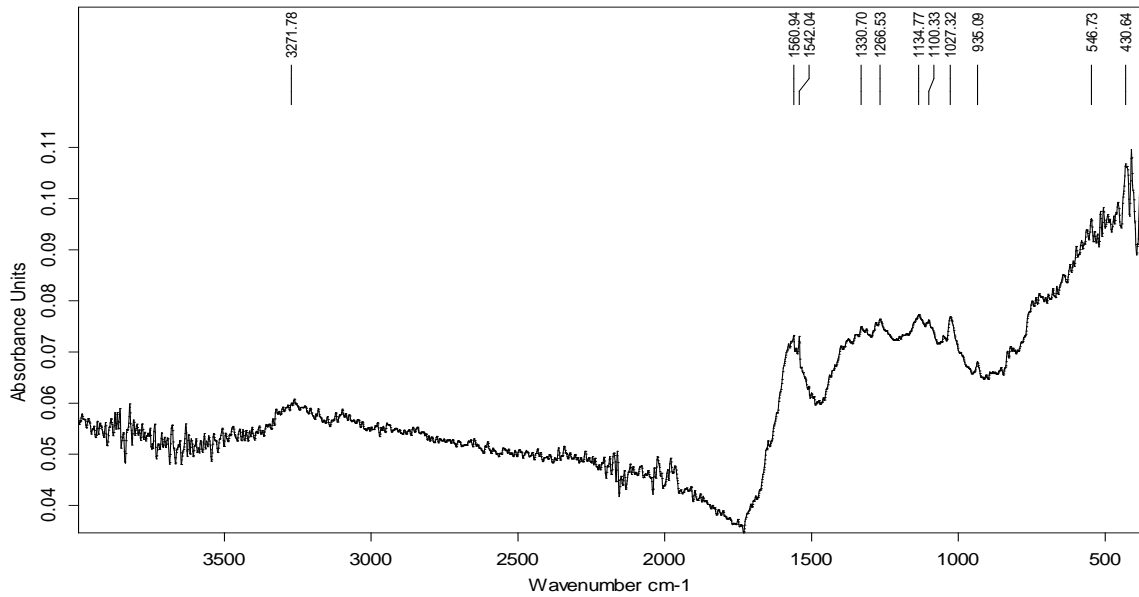


Fig. 1: The FTIR Spectrum of ACZ after adsorption

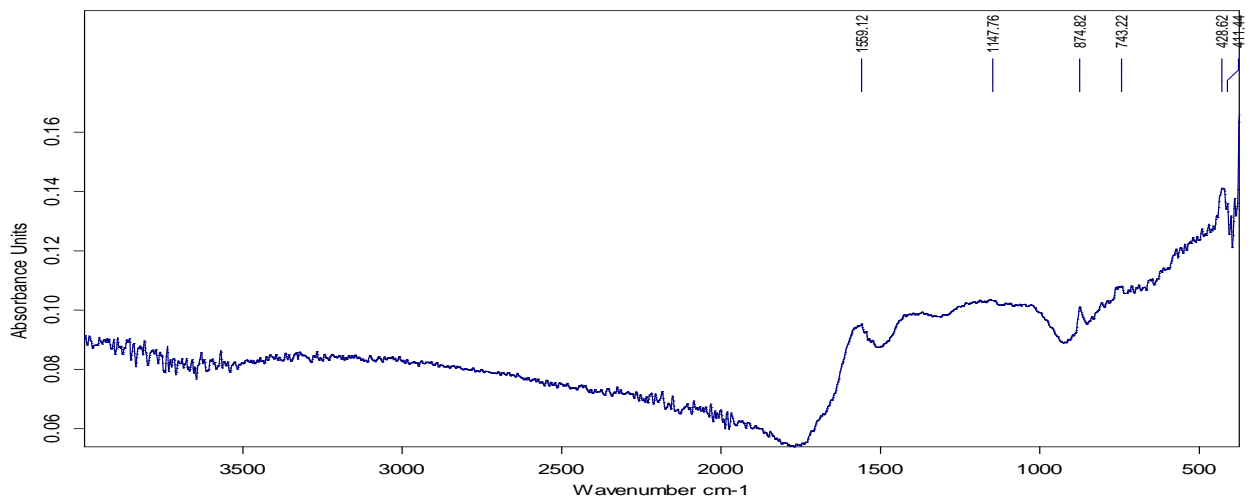


Fig.2: The FTIR Spectrum of ACK after adsorption

From the figures 1 and 2, the pick at 3321 cm^{-1} corresponds to O-H stretching vibration mode in the ACZ. The band at 1574 cm^{-1} can be attributed to the stretching of carbonyl group C=O, the band at 1416 cm^{-1} can also be attributed to the stretching group of N-H.

The band observed at 753 cm^{-1} and 573 cm^{-1} assimilable O-K [10].

After adsorption with activated carbon (ACK), the vibration elongation grouping of O-Cd was observed. And After adsorption with activated carbon (ACZ), the band at 1542 cm^{-1} was attributed to the stretching of C-Cd with rearrangement of π electron graphene of the activated carbon confirming the presence of Cd(II) ions adsorption onto activated carbon.

Adsorption parameters

Effect of Contact Time

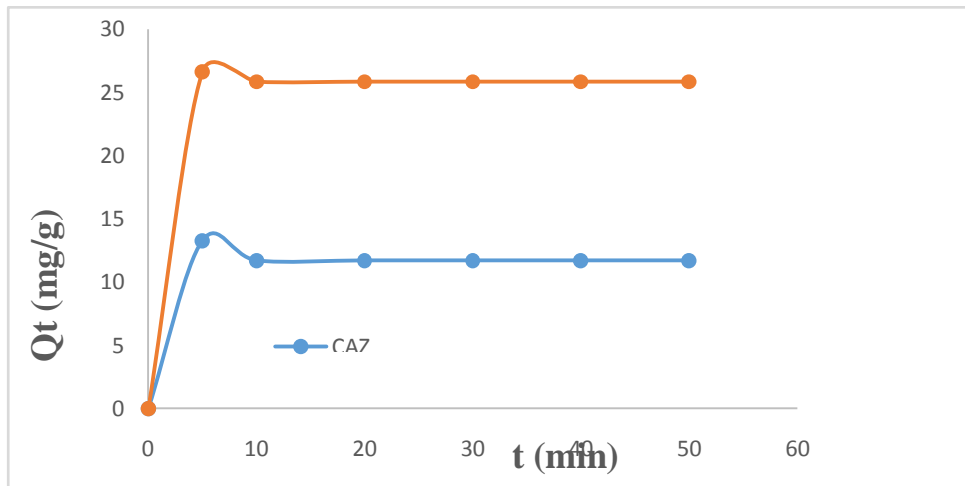


Fig.3. Effect of agitation time on the adsorption of cadmium(II)ions on ACZ and ACK

The effect of contact time of both adsorbent was determined by agitating 0.01 g of adsorbent in 20 mL solution of cadmium(II) ions with initial concentration of 120 mg.L^{-1} . Adsorption of these ions was very fast between 5 to 10 minutes because of the available vacant sites at the

surface of the adsorbent. The quantities adsorbed were 26.639 mg/g for ACK and 13.280 mg/g for ACZ. After 10 minutes for both adsorbents, the adsorption of cadmium(II) ions became constant, this might be due to the saturation of active sites present at the surface [9].

Effect of Adsorbent dose

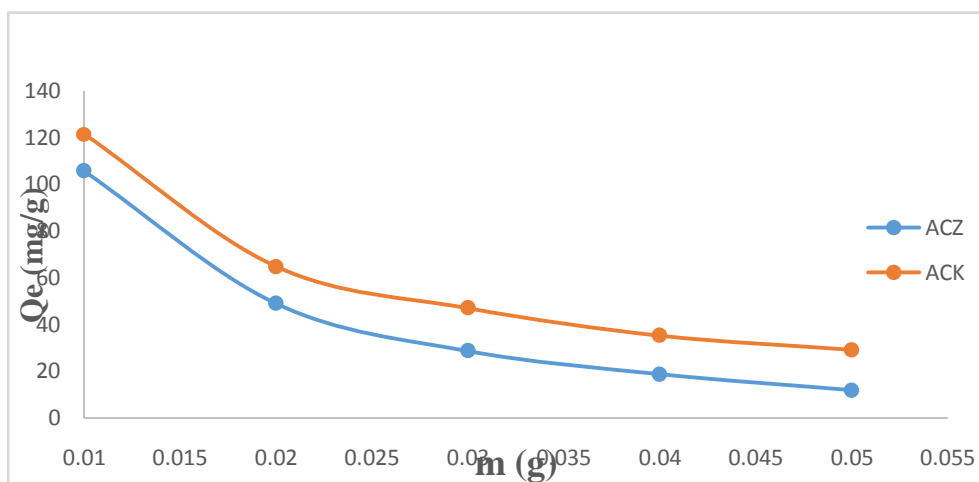


Fig.4. Effect of Adsorbent dose on the adsorption of Cadmium(II)ions on ACZ and ACK

The study of the effect of adsorbent dose on the adsorption of cadmium(II) ions were carried out with different adsorbent mass varying from 0.001 to 0.005 g at initial concentration of 120 mg.L⁻¹. The adsorption capacities of cadmium(II) ions by ACZ and ACK were found to decrease by increasing the adsorbent dose. This might be due to the agglomeration of the particles which form aggregates and

obstruct the pores and thus prevent intra-particle diffusion into the pores of the carbon. This agglomeration reduces the electrostatic force between the adsorbate and adsorbent and disguises the adsorption sites. In addition, the decrease in adsorption capacity may be also due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles.

Effect of initial pH

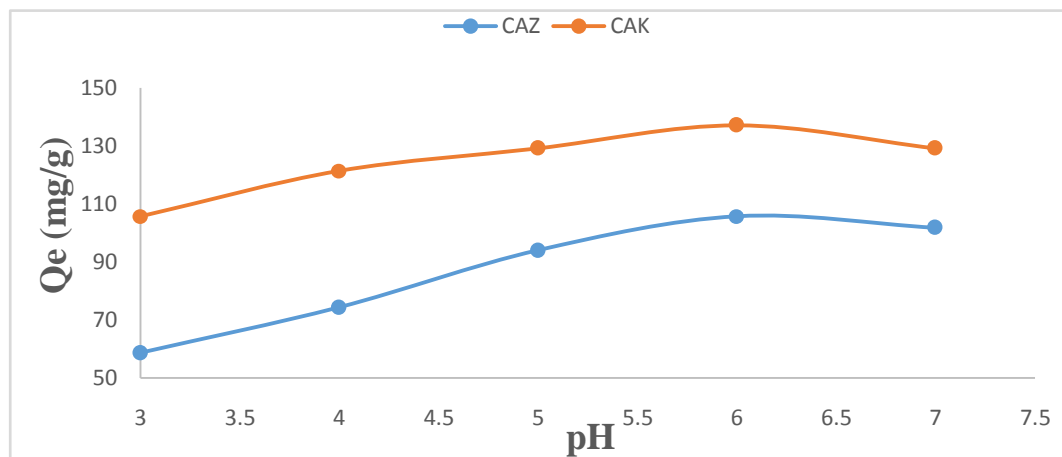


Fig.5. Effect of pH on the adsorption of cadmium(II) ions on ACZ and ACK

It is known that the adsorption of heavy metal ions depends on the pH of the solution. The pH range of the solution was varied between 3 and 8. It was found out that at the low pH the quantities of cadmium(II) ions adsorbed were inhibited. This can be explained by the competition between the hydrogen ions and cadmium(II) ions on the sorption sites. Or from the basis of pH_{zpc} . The pH_{zpc} of ACZ and ACK are 5.3 and 7.4 respectively. At

pH lower than pH_{zpc} , the surface of the adsorbents becomes positively charged therefore increasing the electrostatic repulsion between the adsorbents and the cadmium(II) ions thus reducing the adsorption quantity [16].

At high pH = 6 the quantities adsorbed are also high, firstly for the ACZ, the electrostatic attraction strength between adsorbate and adsorbent increases because pH_{zpc} (5.3) is less than 6 and same to ACK

Effect of initial concentration

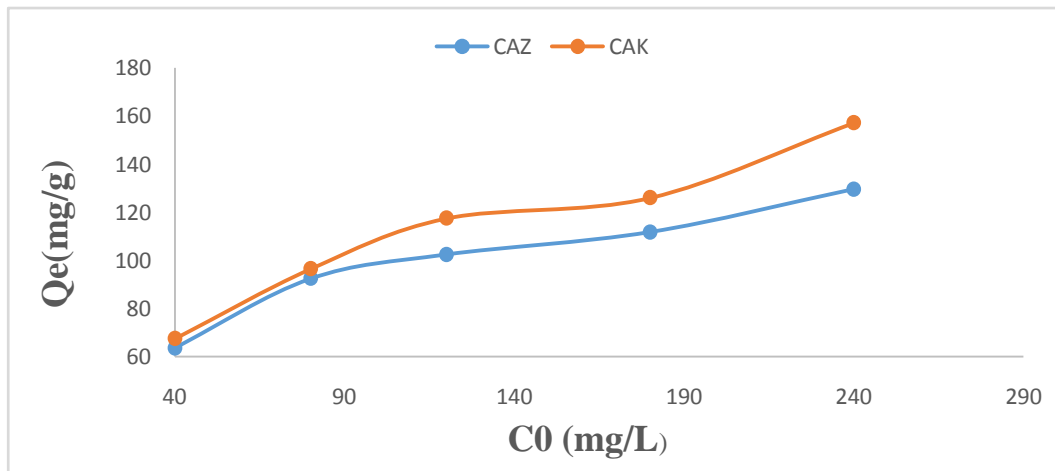


Fig.6. Effect of the initial concentration on the adsorption of cadmium(II)ions on ACZ and ACK

The equilibrium adsorption capacities of the adsorbents obtained from experimental data at different initial cadmium(II) ions concentrations are presented in fig. 6. The concentration of the adsorbate increases with adsorption quantity. This might be due

to the increase in collision forces between metal ions in solution [17], which breaks the resistance forces on the surface of both adsorbents thus facilitating the diffusion of cadmium(II) ions into the pores [18].

Effect of inorganic salts

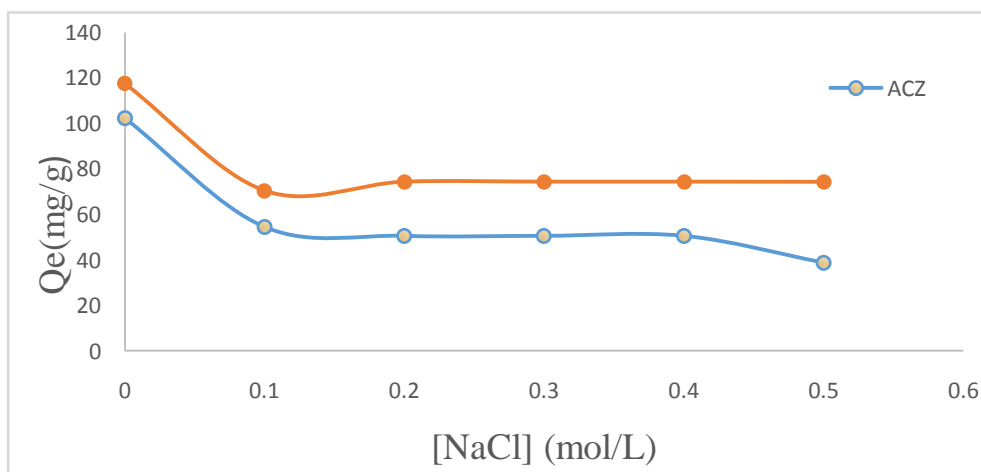


Fig.7. Effect of inorganic salts on the adsorption of cadmium(II) on ACZ and ACK

Fig.7 shows that the adsorbed quantities of Cd^{2+} ions decrease with

increase of salt concentration in solution. This can be explained by the fact that when

NaCl concentration increases, there is wave interference between Cd^{2+} ions and Na^+ ions. From the atomic point of view, Na^+ which has a weak atomic weight than Cd^{2+} will be mobile and would diffuse more easily on the material surface [19]. The Na^+ ions occupy a huge number of active sites that the diffusion of Cd^{2+} ions inside the pores becomes very difficult. So the more higher the concentration of Na^+ ions increases in the solution the

smaller the quantities of Cd^{2+} ions adsorb because of the electrostatic repulsion between Na^+ ions and Cd^{2+} ions as discussed earlier.

Adsorption isotherms

Adsorption of Cd^{2+} ions by ACZ and ACK was modelled using the Freundlich, Langmuir, Tempkin, and Dubinin–Radushkevich (D–R) isotherms with the quality of the fit assessed using the correlation coefficient, R^2 .

Table 2: Isotherms models parameters

Isothermes	Paramètres	Adsorbants	
		ACZ	ACK
Langmuir	R^2	0.954	0.919
	Q_m (mg/g)	116.279	138.889
	R_L	0.029	0.027
Freundlich	R^2	0.970	0.992
	K_F ($\text{mg}^{11/n} \cdot \text{L}^{1/n}/\text{g}$)	41.149	41.075
	$\frac{1}{n}$	0.214	0.258
D--R	R^2	0.8241	0.8612
	Q_m (mg/g)	109.717	129.451
	$K' \times 10^6$ (mol^2/J^2)	7.000	5.000
	E (kJ/mol)	267,261	316.228
Tempkin	R^2	0.951	0.952
	B (J/mol)	127.848	93.117
	A (L/g)	3.125	1.611

The slope and intercept of plots of C_e/q_e versus C_e , were used to calculate q and Langmuir isotherm parameters (Table 2) for Cd^{2+} ions adsorption on ACK and ACZ yielded isotherms that were in good agreement with observed behavior ($R^2 \geq 0.95$ and $R^2 \geq 0.91$) respectively for ACZ and ACK. The values of R_L are 0.029 for ACZ and 0.026 for ACK. These results show that the adsorption is

favorable for the both adsorbents. The cadmium(II) ions adsorption capacity were 116.279 and 138.889 mg g^{-1} for ACZ and ACK respectively. These quantities were higher than the adsorption capacity of other low cost adsorbents [21].

The Freundlich isotherm constants K_F and n were determined from the intercept and slope of a plot of $\log q_e$ versus

$\log C_e$. In this study n values are greater than unity indicating chemisorption [12]. An isotherm with $n > 1$ is classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption [15]; [20].

Linear plots for Tempkin adsorption isotherm, which assumes chemisorption of an adsorbate onto the adsorbent, fitted quite well with correlation coefficients ≥ 0.95 for the both adsorbents (Table 2). This further supports the findings that the process of adsorption of

cadmium(II) ions onto ACZ and ACK is chemisorption [14].

D-R model show the high energy ($>200\text{Kj/mol}$) which characterizes chemisorption process.

Kinetics studies

Four kinetics models were used to fit the experimental data amongst which included the pseudo first-order, pseudo-second order, Elovich and intraparticle diffusion model. The results are presented in the table below.

Table 3: Kinetics models parameters

Adsorbants		CAZ	CAK
Pseudo-First Order	$K_1 (\text{min}^{-1})$	-0.0006	-0.0005
	R^2	0.343	0.343
Pseudo-Second Order	K_2	0,449	0,832
	$(\text{G} \cdot \text{min}^{-1} \cdot \text{m}^{-1})$		
	$Q_e (\text{mg/g})$	11.655	25.840
	R^2	0.999	1.000
Elovich	B	-3.598	-1.797
	A	-1.282×10^{-11}	-3.504×10^{-43}
	R^2	0.585	0.585
Diffusion Intraparticulaire	K_{id}	28.451	55.852
	A	0.045	0.011
	R^2	0.785	0.785

The results show that, the pseudo-second order kinetic model is favorable for the adsorption of cadmium(II) ions from aqueous solution onto ACZ and ACK with $R^2 > 0.999$. Intraparticle diffusion shows that the ACK is better than ACZ for adsorption of Cd^{2+} ions because the constant of diffusion is > 50 for ACK. [21].

Comparative study of the adsorption of cadmium(II) ions

The obtained results were compared to other results of the adsorption of cadmium(II) ions with other adsorbent and the results presented in table 4. From these results, it can be observed that these two adsorbents are better for adsorption than the other adsorbents.

Table 4: Comparison of Adsorption Capacity of Cadmium(II) Ions with others

Adsorbents	Adsorbents Q_m (mg/g)	References
Montmorillonite	0.150	Ecboonet <i>et al.</i> , 2010
Rice Husk Ash	3.84	El-Said <i>et al.</i> , 2010
KAO.1; MKB7.407 ;	9.174	Essombaet <i>et al.</i> 2014
ACZ	116.279	Present study
ACK	138.889	Present study

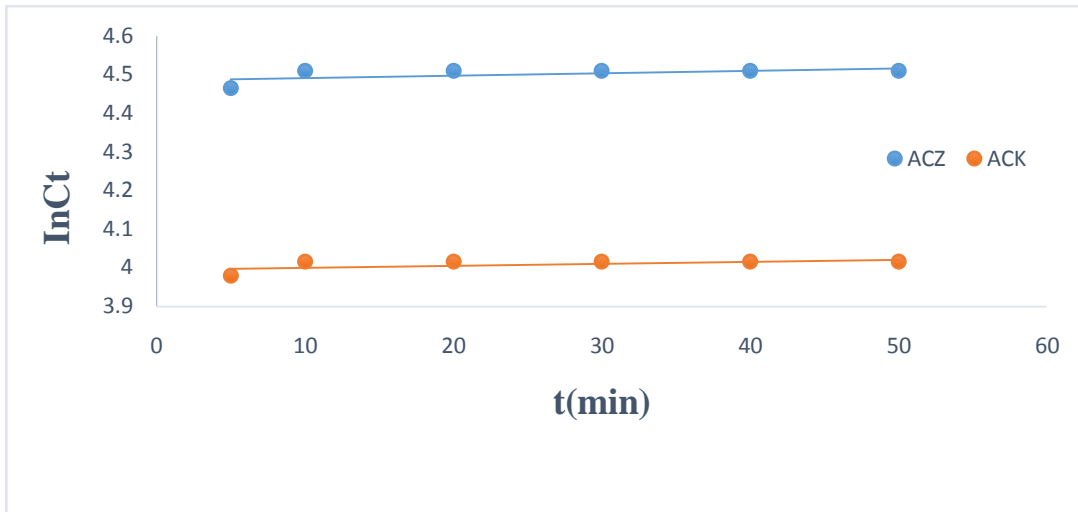


Fig. 8: Linearized pseudo-first-order plot

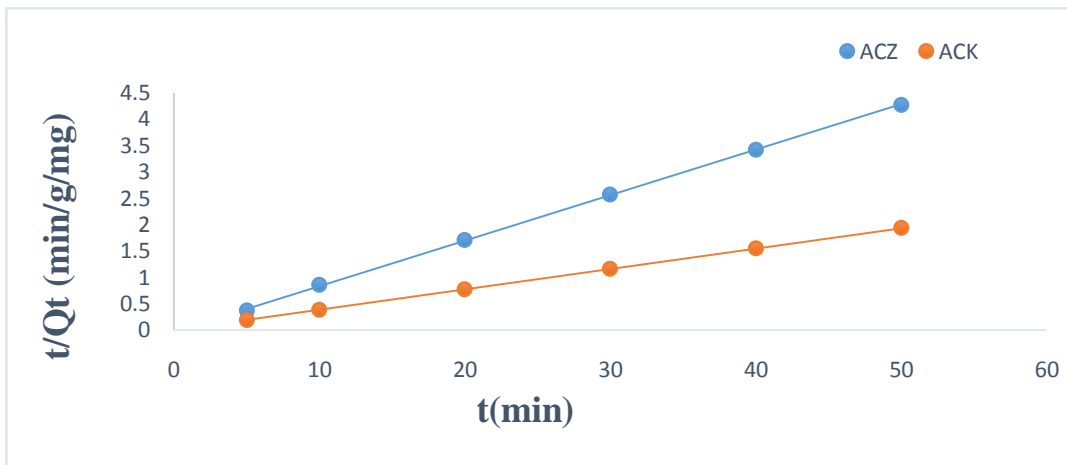


Fig.9: Linearized pseudo-second-order plots

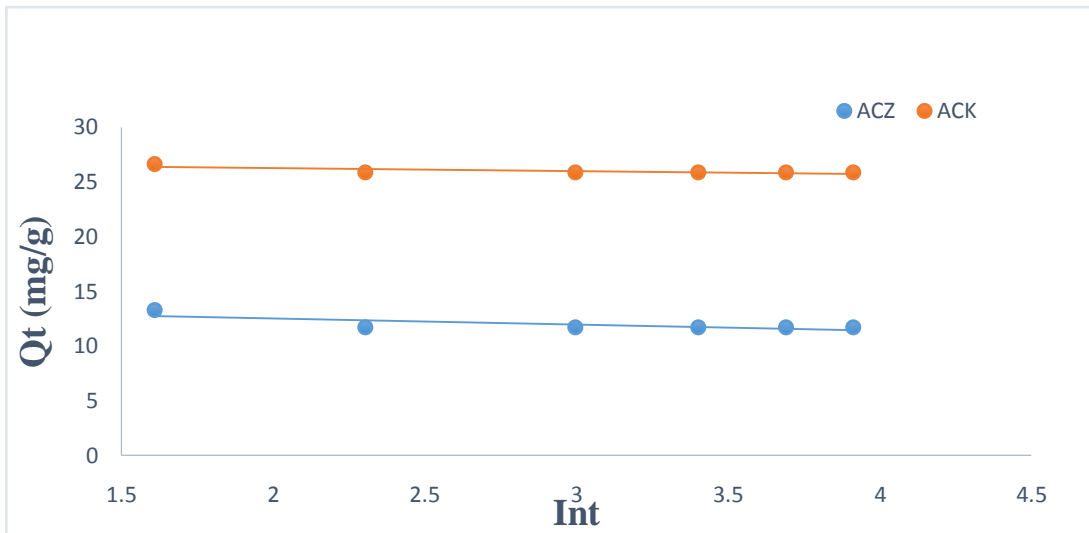


Fig.10:Linearized Elovich plots

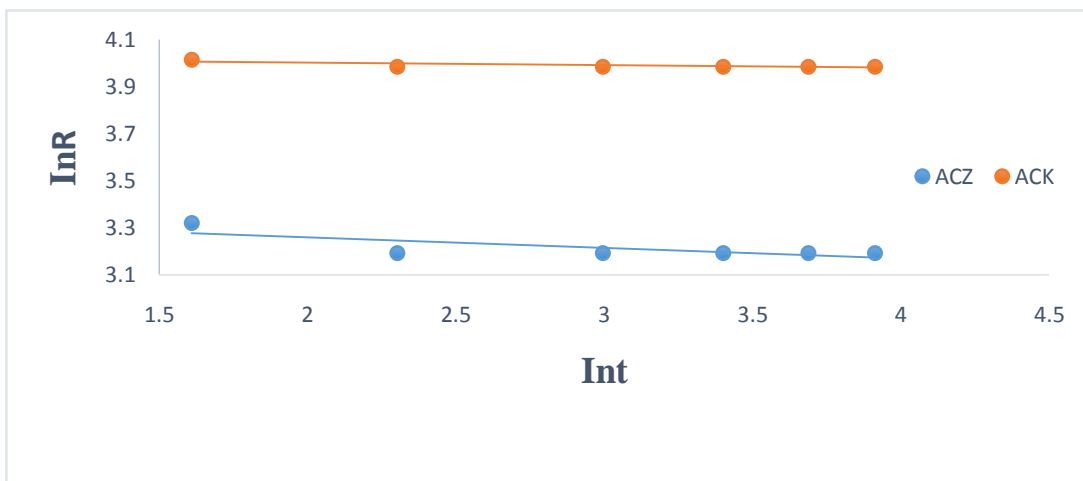


Fig.11:Linearized intraparticle diffusion plots

CONCLUSION

In this study, the ability of ACZ and ACK for the adsorption of cadmium(II) ions from aqueous solution has been explored. The extent of removal depended on the concentration of the adsorbate, pH, contact time, and adsorbent amount. The sorption capacity increased with an increase in the initial cadmium(II) ions concentration at an

optimum pH of 6. Isotherm models show that adsorption of cadmium(II) ions on both adsorbents in the first case showed monolayer coverage according to Langmuir isotherm and secondly multilayer coverage according to Freundlich and Tempkin isotherms. Furthermore, linear regression of the experimental data showed that cadmium(II) ions adsorption best fitted the

pseudo-second order model characterizes chemisorption adsorption process. The intraparticle diffusion model shows that ACK is better than ACZ for the removal of cadmium(II) ions from solution. Ionic strength shows that the inorganic salt has a significant influence on the adsorption of cadmium(II) ions.

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