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ADSORPTION OF Cd(II) AND Pb(II) IONS FROM AQUEOUS SOLUTION USING UNMODIFIED AND MODIFIED ADSORBENTS PREPARED FROM DESERT DATE PEELS (*Balanites aegyptiaca*)

Mamman Ibrahim Alkali^{1*}, Nasir Abdus-Salam², Musa Rabi Abdullahi³, Esther Ville¹ and Mohammed Kyari Dikwa⁴

¹Department of Chemistry, Borno State University, Nigeria

²Department of Chemistry, University of Ilorin, Nigeria

³Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria

⁴Department of Pure and Applied Chemistry, University of Maiduguri, Nigeria

***Corresponding Author's Email Address:** ibrambnanabe@gmail.com

ABSTRACT

The problem of poor or non-treatment of wastewater is often attributed to high cost of purification methods in our industries. Therefore, there is the need to provide alternative adsorbent of comparative effectiveness but develop from agro-based waste. The purpose of this research was to provide understanding of the mechanisms for the adsorption of Cd(II) and Pb(II) ions from aqueous solutions onto Desert Date peels as adsorbent. This was done through characterization and optimum adsorption conditions of Unmodified and Modified Desert Date Peels (UDD and MDD). A 3 M ZnCl₂ was used for the modification of the desert date peel. The results for Fourier-Transform Infrared Spectroscopy (FTIR) of UDD and MDD spectra show broad band peak at 3448.84 cm⁻¹ and 3414.12 cm⁻¹ which corresponds to O-H stretching mode of hydroxyl groups on the surface of the activated carbon. The maximum adsorption capacity of Cd(II) and Pb(II) ions onto UDD and MDD are 94.06 and 80.56 mg/g being observed within 60 min. The adsorption isotherm study ascertains a good correlation coefficient which Langmuir isotherm fitted well into UDD and MDD with (R²) values 0.9893 and 0.9668 and UDD obeyed pseudo second order kinetics model. Thermodynamic studies revealed that the adsorption system was feasible, non-spontaneous and endothermic 6.684 and 8.675 kJ/mol for Cd(II) and Pb(II) ions respectively. The results showed that, both UDD and MDD have the potentials to be applied as alternative low-cost adsorbents in the remediation of heavy metal ions from aqueous solution.

Keywords: Adsorption; Kinetics; Isotherms; Desert Date peels; Thermodynamics

INTRODUCTION

Environmental pollution has become progressively flamboyant with the continuous innovations in technology across the globe [1]. The release of effluents from chemical industries such as textile, pharmaceuticals and cosmetics to the surface water are causing a serious challenge on human health, plants as well as microorganism [2]. Consequently, many conventional methods are used for the removal of toxic metals from aqueous solutions such as, liquid to liquid extraction [3], coagulation [4], filtration [5], reverse osmosis [6,7], electrochemical treatment [8], membrane process [9], chemical precipitation [10], evaporation recovery [11,12], Ion-exchange [7], advanced oxidation processes [13], cavitation technology [13], electrocoagulation [14]. Forward osmosis [15,16] and flocculation [17]. Among these treatment options, adsorption appears to have considerable potential for the removal of toxic heavy metal ions from industrial effluents [18,19] because considered to be economical, cost-effective, easy operation and efficient technology as many adsorbents can be provided by forestry and agricultural residues (normally biomass) with one method of “dealing with waste by waste” [11,18,19].

Adsorption onto activated carbons is an effective and acceptable technique for metal ions and other micro-pollutants removal. Adsorption is a process that occurs when gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent) forming a molecule or atomic film (adsorbate). It is different from absorption in which absorption occurs when a substance diffuses into a solid to form a solution [20]. However, the use of natural agro-based waste materials is a promising alternative because of their relative abundance in the environment [21,22].

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic at low concentrations [23]. Examples of heavy metals include chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg), copper (Cu), cobalt (Co), zinc (Zn) among others. Heavy metals are chemical species which may cause severe damage to the planet's entire ecosystem. Since they are not biodegradable, they accumulate during the years within the environment and in living beings [19]. The contamination of water resources by heavy metals is highly relevant due to the fact that they dissolve within this matrix and immediately become available to the living beings in the ecosystem. The intake of contaminated water by humans and animals affects the entire food chain [24,25].

Wastewater from textiles is mostly not free from toxic metal contaminants [2]. The toxic metals may come as impurity from the chemicals such as caustic soda, sodium carbonate and other salts used during processing. For instance, caustic soda may contain cadmium, lead among others. Similarly, the effluents produced from dyes stuffs, constitutes another problem to the wastewater not only because of their chemical properties but also because of the colours and odours [26,27].

Desert date (*Balanites aegyptiaca*) belongs to the family Balanitaceae. It is a multi-branched, evergreen tree native to the Sudano-Sahelian region of Africa, the Middle East and South Asia [28]. Similarly, the fruit used as oral hypoglycemic drug in the Sahara region of Africa [29]. The fruits are also commonly used as purgative, antiparasitic and schistosomicide [30]. However, desert date peel has no economic value but rather pollute the analytical environment [31].



Fig. 1: Desert date peels (*Balanites aegyptiaca*)

The increase in the use of agriculturally based waste for the preparation of activated carbon is partly due to its availability, low cost, renewable source and it is a way of recycling agricultural wastes which otherwise constitutes environmental pollution [32,33]. However, this research tends to proffer solutions by using this organic waste: unmodified and modified Desert date peels (*Balanite aegyptiaca*) as adsorbent to investigate the adsorption of Cd(II) and Pb(II) ions. The research also investigates the characterization, physicochemical, isotherm, kinetic, and thermodynamic studies.

MATERIALS AND METHODS

Sample Preparation

The Desert date peel used in this research was harvested from Mobbar Local Government of Borno State, North-east Nigeria located between latitude 13.1330° N and longitude 12.7135° E and transported to the laboratory for preliminary treatment before use. The choice of this adsorbent was based on its low cost, considering its abundance in the city and remote areas [31].

Preparation of the Unmodified Adsorbent

The edible parts of the Desert date (*Balanite aegyptiaca*) were removed left behind the peels as waste, which was thoroughly washed with distilled water to remove the impurities according to the method adopted from [34]. The sample was dried at a room temperature for 46 hrs. A 50 g of the sample (Desert date peels) was weighed and transferred into clean a porcelain crucible and was carbonized at 300 °C for 1 hr in a pyrolyser under inert environment by slight method of [35]. The carbonized material was allowed to cool in a desiccator. After cooling, the carbonized material was weighed to determine the percentage carbon yield according to the method adopted from [34].

$$\% \text{ Carbon Yield (CY)} = \frac{\text{weight of the product}}{\text{weight of the starting material}} \times 100 \quad (1)$$

Thereafter, the material was pulverized using mortar and pestle to reduce the size to 0.01 mm particle sizes. Thereafter, the fine carbonized sample was labelled appropriately and kept in polyethylene bottle for batch adsorption experiment according to the method adopted from [36]

Preparation of the Modified Adsorbent

The preparation of modified Desert date peels (*Balanite aegyptica*) involved chemical activation and washing. A 20 g of the dried sample was impregnated with 3 M ZnCl₂ at 1:2 and kept the solution for 24 hr at a room temperature before further action [34].

$$\text{Impregnation ratio} = \frac{\text{weight of the activating agent}}{\text{weight of the carbonizing material}} \quad (2)$$

The modified adsorbent was washed several times with deionized water until neutral pH was obtained [37,38]. The chemically activated sample was dried in an oven at a 105 °C for 1 hr. The dried sample was weighed and taken into pyrolyser in a porcelain crucible and carbonized at 400 °C for 1 hr under N₂ gas after which the samples were transferred into a desiccator to cool. The

chemically activated carbon prepared was weighed to determine the percentage carbon yield Eq. (2) [34].

Characterization Analysis of the Adsorbents

The unmodified and modified adsorbents of Desert date peels were characterized, by using the following equipment: Fourier-Transform Infrared Spectroscopy (FT-IR) for surface functional groups analysis, Scanning Electron Microscopy (SEM) for surface morphology and Energy Dispersive X-ray (EDX) for elemental analysis.

Batch Adsorption Experiment

A Batch experiment was conducted on the adsorbents in order to investigate the effects of initial adsorbate concentration, adsorbent dosage, contact time, pH and temperature for adsorption of Cd(II) and Pb(II) ions [11,19]. The initial adsorbate concentration of metal ions and corresponding concentrations after fixed time periods was measured by atomic absorption spectrophotometer while the metal concentration retained in the adsorbent phase was calculated by Eq. 3

$$q_e = \frac{V(C_i - C_e)}{M} \quad (3)$$

Where q_e = the amount of solute adsorbed from solution (mg/g), V = volume of the adsorbate (L), C_i = the concentration before adsorption (mg/L), C_e = the concentration after adsorption (mg/L) and M = the mass of the adsorbent (g) [18,39].

Effect of Initial Adsorbate Concentration

Several standard solutions with varying concentrations of cadmium and lead ions (200, 400, 600, 800 and 1000 mg/L) were prepared. A 20 ml of these solutions was added to 0.01 g of the adsorbents in different 100 cm³ conical flasks and agitated using a thermostat mechanical agitator at 230 rpm for 5 hr each. This was done in duplicate. At the end of the time, the contents of the flasks were filtered and analyzed by using atomic absorption spectrophotometer [18,19]. Eq. 3 was applied to calculate the quantity of adsorbed.

Effect of Adsorbent Dosage

A 20 mL each of the metal ions solutions was added to various amount of the adsorbent (0.01, 0.02, 0.06, 0.08 and 0.1 g) in a different 100 mL conical flasks, flasks were corked and agitated for 5 hr on a thermostat mechanical shaker at 230 rpm. The content of the flasks was filtered and analyzed by using atomic absorption spectrophotometer [18,19] Eq. 3 was applied to calculate the quantity adsorbed.

Effect of Contact Time

A 20 mL each of stock solution of the metal ions solution was transferred into different 100 cm³ Erlenmeyer flask, corked and labelled. A 0.01 g each of the adsorbents was weighed into the different labelled flasks and agitated in a mechanical shaker for different contact times (10, 20, 30, 60, and 90 min). This was done in triplicate. After each agitation time, the content of each flask was then filtered. The equilibrium concentration of the metal in each of the filtrate was determined by using atomic absorption spectrophotometer [18,19]. The quantity adsorbed was calculated from Eq. 3.

Effect of pH

A 0.01 g of each of the adsorbents was contacted with optimal concentration of metal ion solution, varying initial pH values (3, 4, 5, 6, 7 and 8) and keeping optimal conditions of time and temperature. The pH was adjusted with 0.1 M NaOH/ 0.1 M H₂SO₄ to the desire pH. At the end of contact time, the final pH was measured to determine whether the working pH changes significantly

or not. The reactor content was filtered and analyzed for unadsorbed metal ion by using atomic absorption spectrophotometer [18,19]. The quantity of adsorbed was calculated from Eq. 3.

Effect of Temperature

A 20 mL each of standard solutions was transferred into various 100 cm³ conical flask containing 0.01 g each of the adsorbents, corked and labelled for different temperatures (40, 50, 60, 70 and 80 °C respectively). The mixture was heated and shaken to the appropriate temperature in a water bath shaker at 230 rpm. At the right temperature and contact time, the content of the each of the flask was filtered and analyzed for unadsorbed metal by using atomic absorption spectrophotometer [18,19] The adsorbed quantity was calculated from Eq. 3.

Adsorption Isotherms

Three isotherm equations were used to find out the relationship between the equilibrium concentration of the adsorbate in the liquid phase and in the solid phase [11,40]. The experimental data were substituted into the isotherm equations and appropriate graphs, constants and other variables were generated for each of the equations below:

Langmuir Isotherm

Langmuir adsorption parameters were determined by transforming the Langmuir equation into the linear form of Eq. 4:

$$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} C_e \quad (4)$$

Where, C_e = the equilibrium concentration of adsorbate (mg/L) q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), q_m = maximum monolayer coverage capacity (mg/g) and K_L = Langmuir isotherm constant (mg/ L).

The linear Langmuir plots are obtained by plotting $\frac{C_e}{q_e}$ versus C_e and the values of q_m and K_L was computed from the intercept and slope of the graph respectively. The essential features of the Langmuir equation may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter.

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

Where R_L = value indicates the adsorption nature to be either unfavorable, if ($R_L > 1$), linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The K_L = the constant related to the energy of adsorption (Langmuir Constant) and C_e is initial concentration [11,24].

Freundlich Isotherm

The Freundlich model, [41] is perhaps the most widely used non-linear adsorption equilibrium model, which can be shown to be thermodynamically rigorous for adsorption on heterogeneous surfaces. These data often fit the empirical Equation proposed by Freundlich:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (6)$$

Where K_f = Freundlich isotherm constant (mg/g), C_e = the equilibrium concentration of adsorbate (mg/L), q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g) and n = adsorption intensity. For favorable adsorption, n is generally > 1 . The logarithmic form of the Eq. 6 is more useful for fitting data from batch equilibrium studies, and is given by

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

The constant K_f is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ is a function of the strength of adsorption in the adsorption process. If $n = 1$, then the partition between the two phases are independent of the concentration. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption. On the other hand, $\frac{1}{n}$ being above one indicates not favorable [42].

Kinetic Study

The knowledge of the kinetics in adsorption processes helps to determine the rate at which solute molecules from the bulk solution are taken up onto the surface of the adsorbents, the rate determining steps, as well as the mechanism of the adsorption [43]. Consequently, the kinetics of the adsorption of Cd(II) and Pb(II) ions onto UDD and MDD onto were studied from the variation of agitation time experiment using Pseudo-first order, pseudo-second order, second order and Intra-particle diffusion models on the experimental data obtained.

Lagergren Pseudo First Order Kinetics

The Lagergren equation Lagergren, [44] has been one of the most used equations particularly for pseudo first order kinetics:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)t \quad (8)$$

where $k_1(\text{min}^{-1})$ is the pseudo first order adsorption rate coefficient, q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min). The integrated form of the Eq. 8 for the boundary conditions of $t = 0, q_t = 0$ and $t = t, q_t = q_t$, is written as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where q_e and q_t are the values of the amount adsorbed per unit mass at equilibrium and at any time t . The values of k_1 can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ vs. t .

Pseudo-Second Order Kinetics

The pseudo-second-order equation assumes that the rate limiting step might be due to chemical adsorption [45]. According to this model, adsorbates can bind to two binding sites on the adsorbent surface and the Eq. 9 can be expressed as shown below.

$$\frac{d(q_t)}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

where k_2 is the second order rate coefficient. The integrated form of the Eq. 10 under the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is given by,

$$q_t = \frac{t}{\left[\left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e}\right]} \quad (11)$$

The linear form of this Eq. 11, it makes it possible to obtain q_e and k_2 ($\text{g mg}^{-1}\text{min}^{-1}$) from the plots of $\frac{t}{q_t}$ vs. t .

$$\frac{t}{q_t} = \frac{1}{\left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) \cdot t} \quad (12)$$

RESULTS AND DISCUSSION

Physicochemical Analysis

The point of zero charge (pH_{pzc}) is the pH at which the total number of positive and negative charges on the surface of the adsorbents becomes zero. This parameter is very important in the adsorption context, especially when electrostatic forces are involved in the mechanisms [46]. The pH_{pzc} is the point where the curve of pH final versus pH initial intersects [47]. The results obtained

are 7.7 for both UDD and MDD respectively. The pH at zero-point charge in both results obtained are above 7.0 as shown in Fig. 2. A pH of solution is greater than pH_{pzc} the surface is positively charged which favors the Adsorption anionic species such as Cd(II) and Pb(II) ions. The pH_{pzc} values obtained are slightly higher than the value of 7.0 value reported by [48].

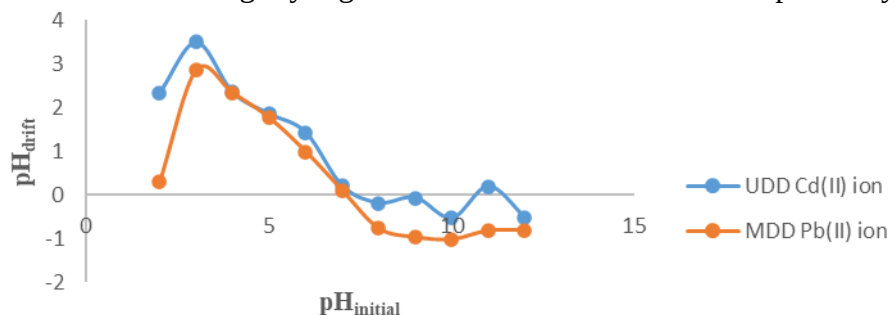


Fig. 2: Graph of pH_{pzc} onto UDD & MDD

Table 1: Summary of some physicochemical analysis of the adsorbents

S/No	Sample Code	Carbon Yield (%)	Bulk Density (g/ml)	pH	pH_{pzc}	Iodine Number (mg/g)	Moisture Content (%)	Ash Content (%)
1	UDD	74.63	0.68	8.73	7.1	523.89	3.16	0.55
2	MDD	69.58	0.97	8.82	7.1	553.89	9.78	1.3

The physicochemical parameters of UDD and MDD are determined and recorded in Table 1. The Moisture content of the UDD < MDD (3.16 and 9.78 %). The ability of an adsorbent to absorb moisture when placed in humid environment suggests good applicability of the sample to adsorption processes [49]. The values obtained were higher than 3.88 % reported by [50]. The low moisture content of the adsorbent predicts that the material could be good for adsorption process [20].

It can be seen from Table 1 that the content of carbon yields of the unmodified adsorbent is higher than modified adsorbent, UDD (74.63 %) and MDD (69.58 %) respectively. This could be attributed to the release of volatiles during carbonization to eliminate non-carbon species [51]. The values obtained were higher than 48.83 % result reported by [50].

It was observed that the ash content analysis in the adsorption process is simply the burning away of organic content, leaving the inorganic minerals [52]. The ash content generally gives insight on overall activity of activated carbon, the lower ash content, therefore, the better the performance of the adsorbent material [53]. The values of the ash content obtained from Table 3.1 are 0.55 and 1.3 % for UDD and MDD. The results obtained are lower than 2.89 % obtained by Abdus-Salam and Buhari, (2016).

The results of iodine number are shown in Table 1 (523.89 and 553.89 mg/g) for UDD and MDD respectively. The modified Desert Date (MDD) with 3 M 1:2 ZnCl_2 showed higher iodine values when compared with unmodified Desert Date (UDD). This could be attributed to the fact that ZnCl_2 is an activation agent that results in a high yield and as well as high surface area [11]. And the value reported was lower than that of 862 m^2/g [23].

Characterization Results

Fourier Transform Infrared spectroscopy (FT-IR) is an essential tool to identify the surface functional groups which can contribute significantly to or enhance adsorption efficiency of the activated carbon by surface complexation [54]. The FTIR SHIMADZU 8400 series was used for analysis and it was carried out in Chemistry Department laboratory, Redeemer University, Osun

State, Nigeria. The samples spectra were recorded over the range of 400-4000 cm^{-1} as shown in Figs. 2 a & b respectively.

The broad band peak of UDD at 3448.84 cm^{-1} corresponds to O-H stretching mode of hydroxyl groups of unmodified adsorbent. Another interesting band at 1620.26 cm^{-1} which could be related to C=O carboxyl group [11,55]. Similar results have been reported by [56] on desert date seed activated carbon. Similarly, the FTIR spectra of the MDD shows presence of weak peak of O-H group was observed at 3414.12 cm^{-1} could be attributed to strength of ZnCl_2 which act as a dehydrating agent on the precursor [57]. A weak peak has been observed at 2920.32 cm^{-1} characteristic of C-H attributed to asymmetric stretching vibration peculiar to aliphatic and aromatic (sp^3) stretching vibration functional groups [58]. Consequently, clear depicts of peak at 1577.82 cm^{-1} which could be related to the C=C stretching bond on the surface of the adsorbent [36,48]. These groups were expected to form strong surface complexes with metal ions [59]. The prominent peak band at 1431.23 cm^{-1} is characteristic of C-O asymmetric stretching [60].

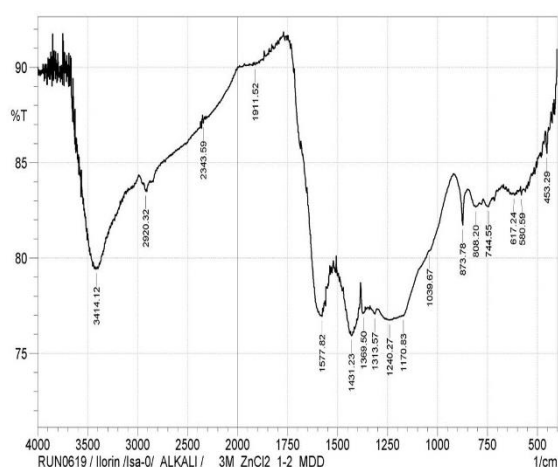


Fig. 3a: FTIR Spectrum of UDD Peels

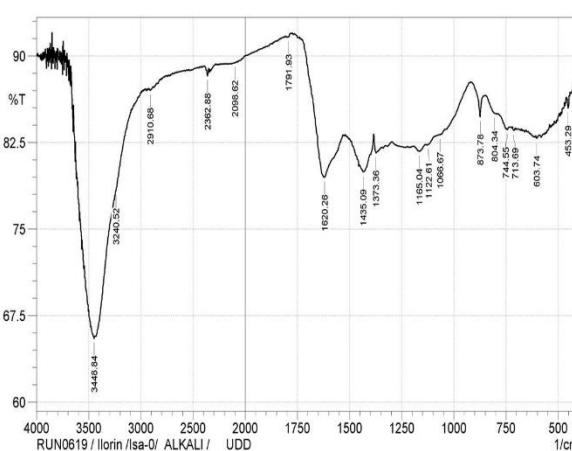


Fig. 3b: FTIR Spectrum of MDD Peels

Table 2: Summary of the assignment of some major peaks on the samples

S/No	Samples	Frequencies (cm^{-1})	Assignment
	UDD	3448.84	O-H Stretching vibrations
		1620.26	C=O Carbonyl group
	MDD	3414.12	O-H Stretching vibrations
		2920.32	C-H asymmetric stretching vibrations
		1577.82	C=C stretching bond
		1431.23	C-O asymmetric stretching vibrations

The SEM micrograph of UDD peels and MDD are presented in Figs. 4 a & b respectively. It can be seen that UDD peels showed lamellar stratified surface, cavities and pores on the activated carbon sample with several large clusters of mesopores spotted on it which revealed that it is highly porous and it is similar to what was earlier reported by [61]. Similarly, the structure of MDD looks like thin sheet or layers with larger porosity on the surface when compared with UDD, this could be ascribed to the fact that zinc chloride had positive impact on the pore size and porosity on the adsorbent [62].

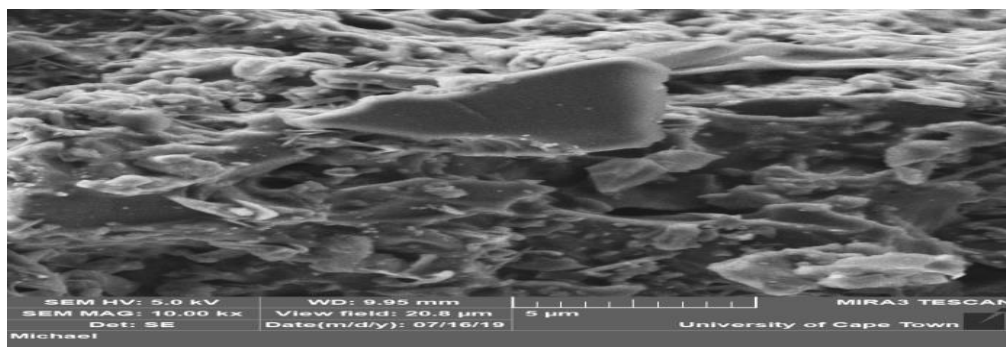


Fig. 4a: SEM Micrograph of UDD peels

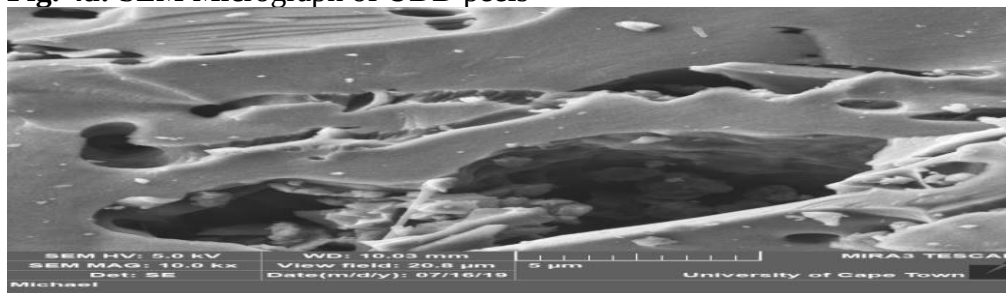


Fig. 4b: SEM Micrograph of MDD

Energy Dispersive X-ray (EDX) microanalysis was used qualitatively to determine the elemental composition of the unmodified and modified adsorbents and the results are presented in Table 3. It could be observed from the Table 3 that carbon and oxygen content are the predominant (85.6 & 83.66 % carbon and 13.67 & 14.6 % oxygen) onto UDD and MDD respectively. The oxygen atom can be of strong effects on the adsorption of contaminants, especially when it is present on the available carbon surface [63]. However, the effect of zinc chloride used as activating agent was also observed in small quantity.

Table 3: Summary of elemental composition of the samples

S/No.	Samples	C	O	K	Si	Ca	Zn	Total (%)
1	UDD	85.6	13.67	0.73	-	-	-	100
2	MDD	83.66	14.6	0.19	0.2	0.19	1.16	100

Adsorption studies results

Effect of Initial Concentration

The initial adsorbate concentration is an important parameter in adsorption studies known to provide the necessary driving force to overcome the resistance to the mass transfer between the aqueous phase and the solid phase [64]. The results of UDD and MDD as presented in Fig. 5 which revealed that the maximum quantity adsorbed of Cd(II) ion onto UDD 93.52 mg/g and MDD Pb(II) 80.56 mg/g at 600 and 800 mg/L of adsorbate concentration. It is generally accepted that the mechanism for adsorbed metal removal is related to the surface properties of activated carbons [62,65]. Similar results have been reported by [66].

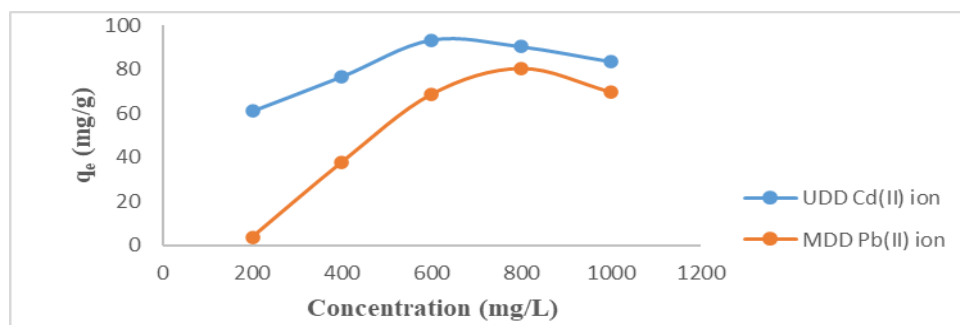


Figure 5: Effect of initial Concentration of Cd (II) and Pb (II) ions on UDD and MDD

Effect of Adsorbent Dosage

Adsorbent dosage determines the amount of adsorbent needed for the removal of a certain amount of heavy metals in wastewater [62]. This was achieved by varying the amount of adsorbent materials from 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 g for Cd(II) and Pb(II) ions onto UDD and MDD and the result was presented in Fig 6. However, the adsorbent dosage of both metal ions adsorbed at lower dosage of 0.01 g which could be related to active adsorption sites and overlapping at lower quantity [67]. Similar results were also obtained from literatures cited by [68,69].

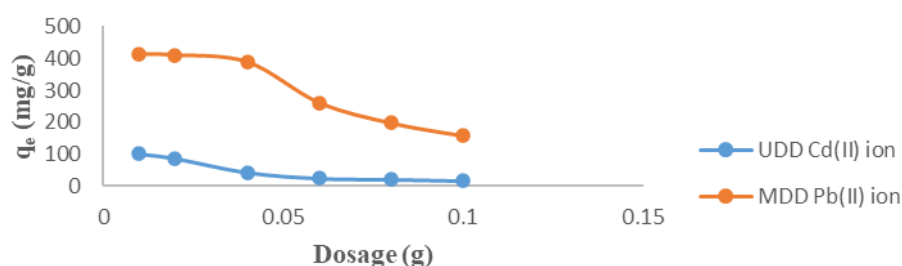


Figure 6: Effect of adsorbent dosage of Cd (II) and Pb (II) ions on UDD and MDD

Effect of Contact Time

The effect of contact time has a greater influence on adsorption phenomena. The effect of contact time helps to understand the rate of reaction and the time of adsorption process reaches equilibrium state [70]. The effect of contact time on the adsorption of Cd(II) and Pb(II) ions are investigated at different time intervals in the range of 10-90 min and the results were presented in Fig. 7 for Desert date peels. The maximum quantity adsorbed at 30 and 60 min for both metal ions could be due to the available number of active sites on the surface of carbons and became slower at the later stages of contact time due to the decreased number of active sites [71]. Similar trend was observed in literature reported by [72].

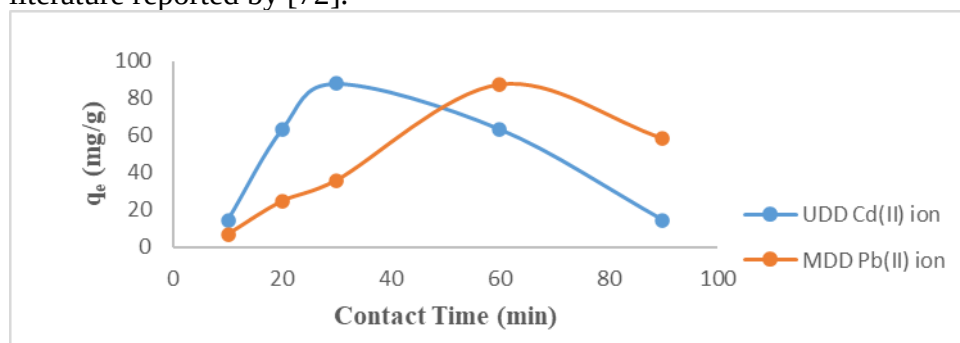


Figure 7: Effect of contact time of Cd (II) and Pb (II) ions on UDD and MDD

Effect of pH

The pH of solution has a significant effect on the uptake metal ions, since it determines the chemistry of surface charge of the adsorbent and degree of ionization as well as speciation of the adsorbate molecules [54,73]. The pH solution governing the targeted metal ions (Cd and Pb) onto unmodified and modified adsorbents are presented in Fig. 8. The adsorption capacity increased sharply when pH increased from 2 to 8 on both adsorbents for metal ions under study. In general, the adsorption capacity showed a declining trend with lower pH values. When the pH of solution is less than pH_{pzc} , the adsorption of anionic species is promoted, whereas, when pH of solution is greater than pH_{pzc} , the adsorption of cationic species is favorable [60]. Consequently, the dependence of adsorption on pH are in agreement with the pH_{pzc} and $pH_{solution}$ in the experiment.

This adsorption behavior could be explained on the basis of surface charge and proton competitive adsorption. At a very low pH, the number of H_3O^+ ions exceed that of the metal ions several times and the surface is most likely covered with H_3O^+ ions, which account for less adsorption [64,74]. When the pH increases, more H_3O^+ ions leave the adsorbent surface making the sites available to the metal ions, which increasingly bind to adsorbent surface through a mechanism controlling electrostatic attraction [47,75]. Moreover, lower H^+ concentration also favors cation adsorption by mass action. For example, the adsorption of bivalent cations such as M^{2+} on cadmium oxide and lead oxide can be written as:

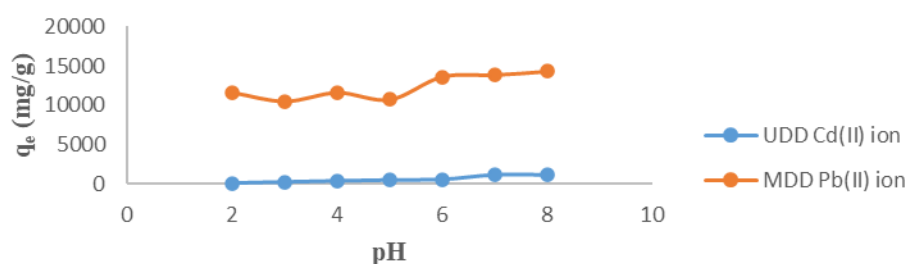


Figure 8: Effect of pH of Cd (II) and Pb (II) ions on UDD and MDD

Effect of Temperature

The effect of temperature plays a significant role in the adsorption context [76]. The effect of temperature on the removal of Cd(II) and Pb(II) ions from aqueous solution onto Unmodified and Modified Desert date peels are investigated by varying the temperature of adsorption between 40 °C to 80 °C. The results are presented in Fig. 9. The maximum adsorption capacity was established at 40 °C and 60 °C for UDD Cd(II) and MDD Pb(II) ions respectively. There are two important effects observed in this adsorption processes. An increase in temperature normally enhances the diffusion rate of adsorbate molecules within the pores of adsorbent due to increased kinetic energy of the solute material and adsorption favors endothermic reaction [72]. Similar trend in the effect of temperature was reported by [77] on adsorption of Malachite green onto eggshell. However, when temperature increases the adsorption capacity decreases which may be related to a decreased equilibrium constant for adsorption at higher temperature. The force of attraction between the adsorbent and the adsorbate ion may have been weakened making the adsorption to decrease. This indicates that the adsorption is exothermic heat of reaction [78]. This behavior is observed on both adsorbents.

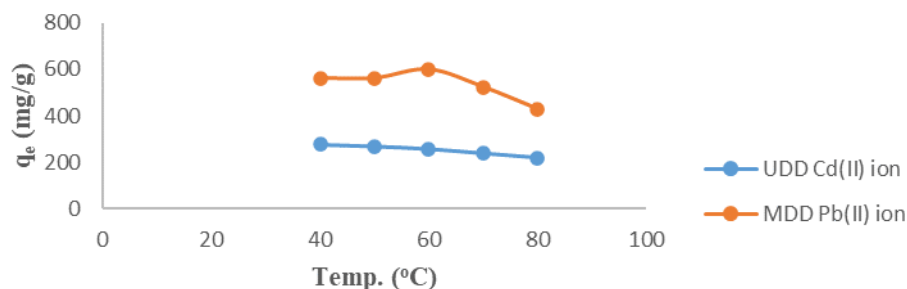


Figure 9: Effect of Temperature of Cd (II) and Pb (II) ions on UDD and MDD

Effect of Adsorption Thermodynamics

The adsorption thermodynamic parameters, such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), were obtained according to equation

$$K_c = \frac{C_s}{C_b} \quad 15$$

$$\Delta G = -RT \ln K_c \quad 16$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad 17$$

where K_c refers to the adsorption distribution coefficient, T represents temperature (K), and R is the universal gas constant. These parameters were obtained from the intercept and the slope from the Van't Hoff plot of $\ln K_c$ against $1/T$ (Abdus-Salam *et al.*, 2021a). The graphs are presented in Fig. 10. The value of ΔG was obtained from Eq. 17

$$\Delta G = \Delta H - T\Delta S \quad 18$$

The values of the relevant significant thermodynamic parameters ΔH , ΔS and ΔG are presented in Table 4. Because ΔH was positive, the adsorption process was endothermic for both adsorbents and the adsorption would be stimulated at a higher temperature to a certain extent [11,19]. The high value of ΔH (> 40 kJ/mol) suggests that the adsorption process is likely to be chemisorption [23,79]. The entropy change ΔS is a measure of the degree of disorderliness and randomness of a system [1,27]. Furthermore, ΔS with negative and this indicates a decrease in the disorderliness and randomness at the adsorbent–adsorbate interface and affinity for adsorbent material [80]. Moreover, the values of ΔG are all positive on both adsorbents. The Gibb's free energy values indicate the degree of spontaneity of adsorption process. This implies a non-spontaneous reaction system over the temperature range studied [81].

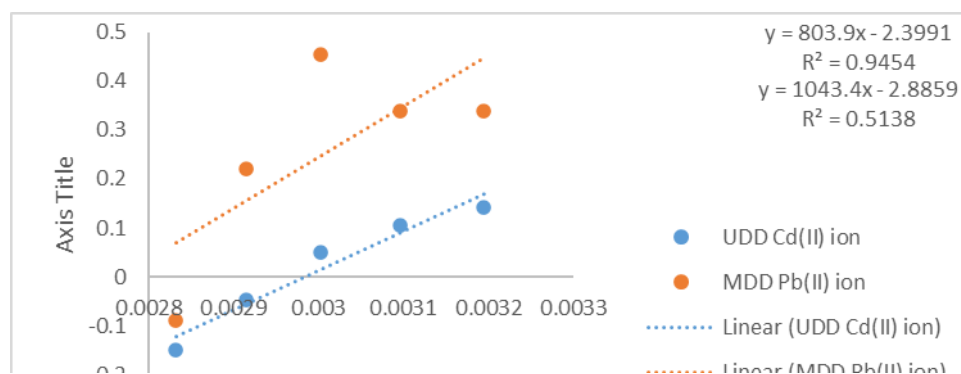


Figure 10: Van't Hoff plot for the adsorption of Cd (II) and Pb (II) ions on UDD and MDD

Table 4: Summary of thermodynamic parameters of the adsorbents

UDD Cd(II) ion				MDD Pb(II) ion		
Temp. (°K)	ΔH° (kJ/mol)	ΔS° (kJ/mol/k)	ΔG° (kJ/mol)	Temp. (°K)	ΔH° (kJ/mol)	ΔS° G° (kJ/mol/k) J/mol)
	6.68362	-0.0199			8.6748	-0.0239
313			12.92797	313		16.1837
323			13.12747	323		16.4236
333			13.32697	333		16.6635
343			13.52647	343		16.9034
353			13.72597	353		17.1433

Adsorption Isotherms

The term Isotherm defines as the relationship between the equilibrium concentration and the amount of adsorbate adsorbed at constant temperature. It can be described graphically how adsorbates interacts with adsorbents using correlation coefficient (R^2) value to understand the conformity of the isotherm model applied with the experimental data. The adsorption is usually modeled by isotherms models which relate the relative concentration of solute adsorbed on that of the solute in solution [11,82]. Summary Isotherm models plots of $\frac{C_e}{q_e}$ versus C_e and $\log q_e$ versus $\log C_e$ of Cd(II) and Pb(II) ions onto Unmodified and Modified Desert date peels are presented in Table 4.

It was observed from Table 4 that the adsorption data fitted best into the Langmuir isotherm model correlation coefficients (R^2) values close to unity are (0.9893 and 0.9688 respectively) in the order UDD Cd(II) > MDD Pb(II) ion. The correlation coefficient suggests that equilibrium data were described Langmuir isotherm model signifying a chemisorption adsorption [83]. However, this observation was further supported by the closeness of experimental data [q_0 (mg/g)] and theoretical values [q_m (mg/g)]. The experimental data q_0 obtained include (90.91 and 80.56 mg/g) onto UDD Cd(II) MDD Pb(II) are close to the theoretical values q_m (90.91 and 76.92 mg/g). The closeness between the experimental data and theoretical values could be attributed to the homogenous distribution of the active sites on the surface of the adsorbents and that the adsorption indicates good monolayer coverage in nature [34]. However, UDD and MDD have barely fitted into Freundlich isotherm and their correlation coefficient (R^2) values are not close to unity given as (0.1371 and 0.5267) presented in Table 5. These adsorbents do not fit into Freundlich isotherm are not multilayer in nature [54].

Table 5: Summary of adsorption isotherm parameters of unmodified and modified desert date peels

Langmuir parameters	UDD Cd (II)	MDD Pb (II)	Freundlich parameters	UDD Cd (II)	MDD Pb (II)
q_0 (mg/g)	96.04	80.56	$\frac{1}{n}$	0.05	0.27
q_m (mg/g)	90.91	76.92	N	19.12	3.64
K_L (L/mg)	0.35	0.03	K_f (mg/g)	0.26	0.07
R_L	4.69×10^{-03}	0.04	R^2	0.14	0.53
R^2	0.98	0.97			

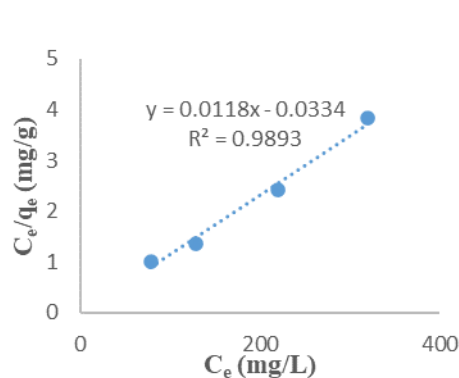


Fig. 11a: Langmuir Isotherm Plot for the Adsorption of Cd (II) ion onto UDD Peels

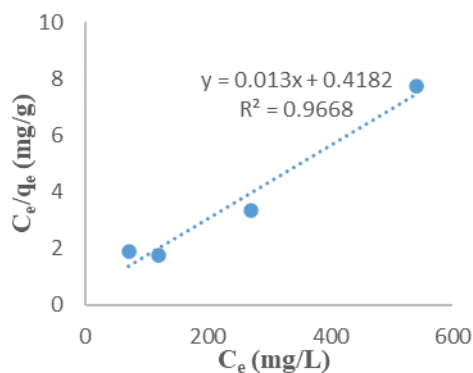


Fig. 11b: Langmuir Isotherm Plot for the Adsorption of Pb (II) ion onto MDD Peels

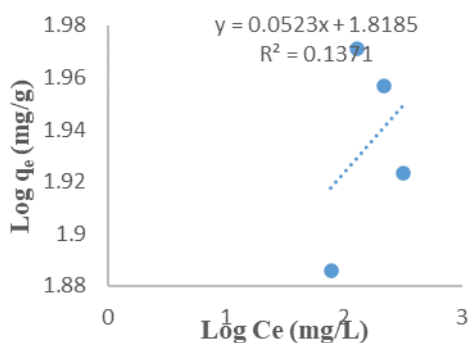


Fig. 12a: Freundlich Isotherm Plot for the Adsorption of Cd (II) ion onto UDD Peels

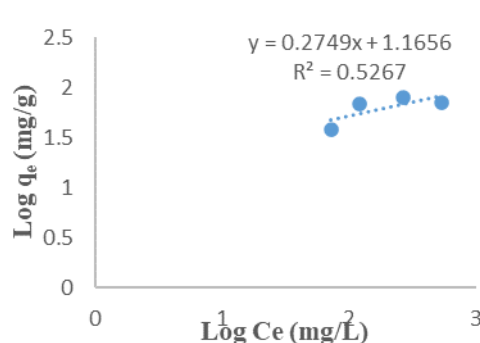


Fig. 12b: Freundlich Isotherm Plot for the Adsorption of Pb (II) ion onto MDD Peels

Adsorption Kinetic Models

The adsorption kinetics provides the rate or speed of adsorbate uptake onto the activated adsorbent within the equilibrium contact time [85]. The Pseudo-first order and Pseudo-second order kinetic models are implemented to evaluate the rate constant of the adsorption process. The linearity of the plots with correlation coefficient values (R^2) that are very close to unity is an indication that the adsorption process followed any of the aforementioned kinetics models [33].

Pseudo-First Order Kinetic Model

The summary of the kinetic parameters for Pseudo-first order and second order are shown in Table 6 for Cd(II) and Pb(II) ions onto Unmodified and Modified Desert date peels respectively. The plots $\log q_e - q_t$ against t and t/q_t against t are presented in Fig. 13

It was observed from Table 5 that the best adsorbents were not satisfactorily fitted well into pseudo-first order using correlation coefficient values (R^2) as evidence as given in the following order; (0.0588 and 0.2441 respectively) onto UDD Cd(II) and MDD Pb(II) ions. It could be concluded that, pseudo-first order kinetic model is not the most suitable model to judge these adsorbents. This reason can be attributed to the fact that pseudo-first order model can only describe the adsorption kinetics of the initial stage and cannot give accurate description and information of the whole adsorption process [72,86]. However, the q_e calculated and the q_e experimental were close to each other in the case of both adsorbents. This could be related to the rate controlling the steps for the uptake of ions is resistance to the boundary layer [87]. These results were in agreement with literature reported by [88] that correlation coefficient on ash and iron nanoparticles showed bad quality of linearization (0.700 and 0.717 respectively).

Pseudo-Second-Order Kinetic Model

Primarily, pseudo-second-order kinetic model is the rate limiting steps of chemisorption involving forces sharing or exchange of electrons between the adsorbate and the adsorbent [68]. The adsorption parameters derived from pseudo-second order kinetic model of Cd(II) and Pb(II) ions onto Unmodified and Modified Desert date peels are summarized in Table 6.

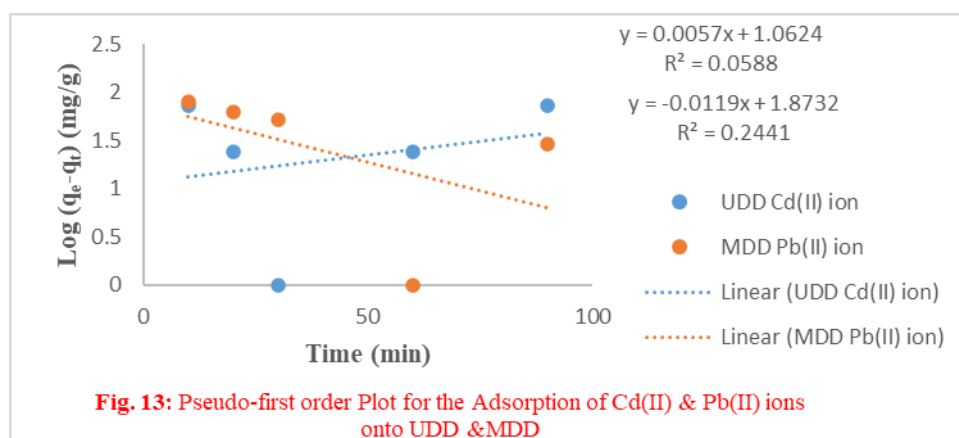
It can be seen from the Table 6 that the degree of correlation coefficient (R^2) is found to be high than correlation coefficient of pseudo-first order. It could be concluded that, both adsorbents fitted satisfactorily into pseudo-second order kinetic model because of the strong interaction between the adsorbent and the adsorbates [22]. However, the q_e calculated of the adsorbents are significantly higher than the q_e experimental values of the pseudo-second order model. This variation could be attributed to adsorbate and adsorbent interaction, transfer of adsorbent particle surface to the intra particle active sites or intra particle precipitation phenomena [89]. This was in agreement with the observation reported by [89].

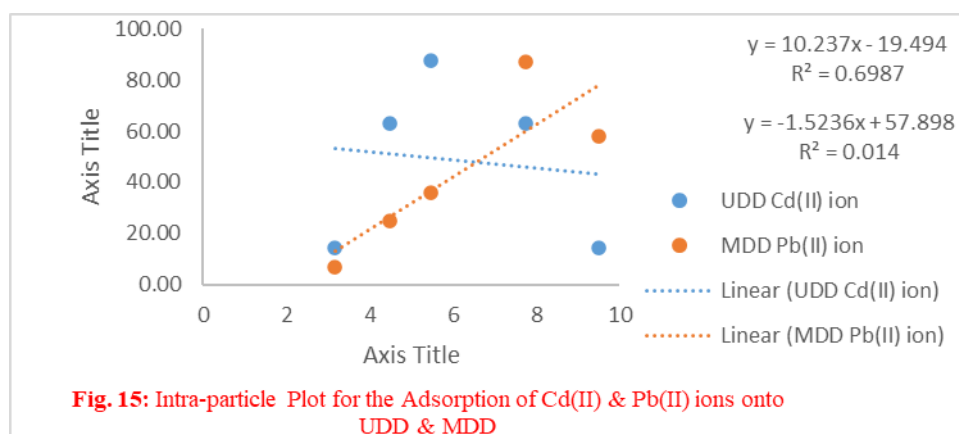
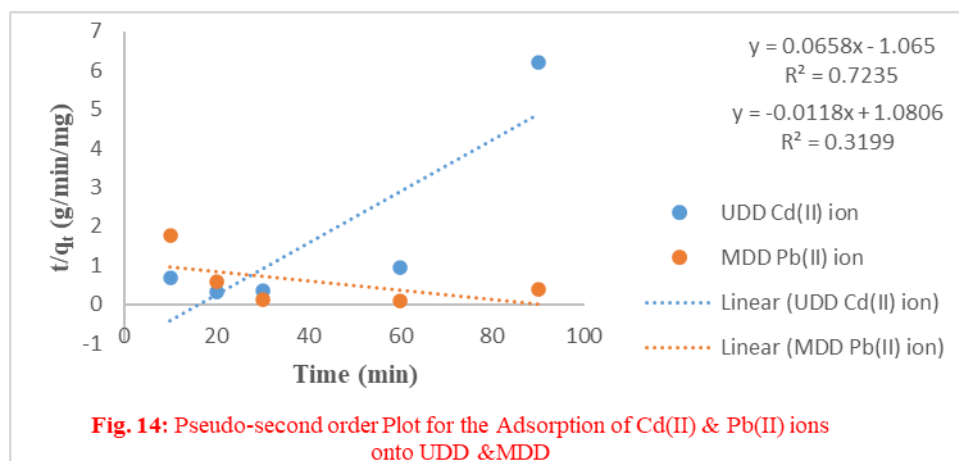
Intra-Particle Diffusion

The determination of the adsorption rate controlling step enhances understanding of the adsorption mechanism [81]. In order to determine the mechanism, kinetic data were tested with Weber's intraparticle diffusion model. From the evaluated parameters in Table 6, C (boundary layer) are 6.52 and 3.16 and correlation coefficient 0.014 and 0.6987 (R^2). The intercept (C) which is the thickness of the surface gives information about the contribution of the surface adsorption in the rate determining step [62]. However, since the intraparticle diffusion plots Fig. 13 did not pass through the origin, it therefore indicated that intraparticle diffusion is not the only rate determining step.

Table 6: Summary kinetic parameters of unmodified and modified desert date

seudo- rst order	DD d(II)	IDD b(II)	seudo-second rder	DD d(II)	IDD b(II)	tra-particle arameters	DD d(II)	IDD b(II)
k_1 (min ⁻¹)	0032	0027	k_2 (g/mg/min)	00047	00008	(mg/g/min ²)	0009	068
q_{exp} (mg/g)	3.04	3.56	q_{exp} (mg/g)	3.04	3.56		516	159
q_{cal} (mg/g)	3.03	4.68	q_{cal} (mg/g)	3.19	44.83	²	014	699
²	0588	2441	²	7235	0574			





CONCLUSION

A locally abundant natural Desert date peels was used for the adsorption of Cd(II) and Pb(II) ions from wastewater under various conditions. The maximum adsorption capacity of the Cd(II) and Pb(II) ions onto UDD and MDD are 96.04 and 80.56 mg/g being observed within 60 min. Increasing pH favored the adsorption of metal ions for both adsorbents. The isotherm study ascertains a good correlation coefficient which Langmuir isotherm fitted well into UDD and MDD. Meanwhile, the kinetics studies indicate a good correlation coefficient for pseudo second order kinetics model onto UDD and MDD respectively. The thermodynamics study showed that the processes are non-spontaneous and endothermic in nature, for both adsorbents. Therefore, the results showed that, both UDD and MDD have the potentials to be applied as alternative low-cost adsorbents in the remediation of heavy metal ions from wastewater.

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