

27 **ORANGE PEEL AS LOW-COST ADSORBENT IN THE ELIMINATION OF Cd(II)**
28 **IONS: KINETICS, ISOTHERM, THERMODYNAMIC AND OPTIMIZATION**
29 **EVALUATIONS**

30
31 **ABSTRACT**

32 The presence of heavy metals in polluted water is known not only to cause stern harm to
33 marine organisms but also to terrestrial plants and animals including human beings. This research
34 applied low-cost and environmental benign adsorbent primed from waste orange peel (OP) in the
35 removal of Cd(II) ions from aqueous solution via the batch process. The surface properties of
36 the orange peel powder was studied using scanning electron microscopy (SEM), energy-
37 dispersive X-ray spectroscopy (XRD) and Fourier transform infrared spectroscopy FT-IR).
38 Operational conditions like temperature, contact time, sorbent dosage, solution pH and initial
39 adsorbate concentration were investigated. The utmost uptake of Cd(II) ion was obtained at the
40 contact time of 120 mins, initial metal concentration of 240 mg/L, adsorbent dosage of 0.04
41 g/L, temperature of 45 °C and solution pH of 5.5 on the adsorption of Cd(II) ion. Equilibrium
42 results showed that the orange peel adsorbent has an adsorption capacity of 27.916 mg/g as
43 obtained from the Langmuir isotherm. The adsorption kinetics data followed a Pseudo-first-order
44 kinetic model with correlation coefficient (R^2) >0.9 and low standard % error values. The
45 adsorption process was found to be spontaneous, feasible and with enthalpy of 0.0046 kJ mol⁻¹
46 and entropy of -636.865 Jmol⁻¹K⁻¹ respectively. Results from the optimization study indicated
47 that higher adsorbent dosage and lower Cd(II) ion concentration increased the percentage of Cd
48 (II) ion removal. Thus, orange peel could be used in the removal of Cd(II) ion from aqueous
49 solutions.

50 **Keywords:** Adsorption, cadmium, equilibrium, kinetics, orange peel,

51 **INTRODUCTION**

52 With the rapid development, industrialization and urbanization, massive volume of sewage
53 sludge, is being produced in the urban areas of major countries of the world including Pakistan
54 (Riaz et al., 2018). Activities in the industry such as tanneries, mining and metal plating can
55 result in the pollution of water system due to the discharge of their by-products many of which
56 contain heavy metals (Brinza *et al.*, 2009; Baysal *et al.*, 2009, Ofudje *et al.*, 2017). While some
57 metals are known to be essential minerals for various biochemical activities, the presence of
58 large or even small amounts of such metals like copper, manganese, lead, cadmium, or zinc, can
59 not only result in severe human health harms but can equally affect the lives of animals and even
60 plants (Brinza *et al.*, 2009; Ofudje *et al.*, 2013). It is well known that the process of heavy metals
61 by human body is very difficult since they are non-biodegradable and as such, they settle down
62 in different internal organs and could lead to serious damage of body system (Gavrilescu, 2004).
63 Cadmium (Cd) has been reported to be one of the most poisonous elements that could be
64 exposed to either in the environment or at work. Also, it can as well accumulate in the human
65 body once absorbed and is efficiently retained throughout life (Bernard, 2008). It is principally
66 poisonous to kidney causing bone demineralization while excessive exposures to cadmium could
67 damage the proper function of the lung and increase the chance of lung cancer (Bernard, 2008).
68 A variety of conventional methods like reverse osmosis, electro-dialysis, ion exchange,
69 adsorption and chemical precipitation have been documented for the elimination of heavy metals
70 from contaminated waters (Ofudje et al., 2020; Ofudje *et al.*, 2017; Gavrilescu *et al.*, 2009;
71 Sadrzadeh *et al.*, 2008). However, some of these methods are expensive, not efficient and
72 sometimes, could lead to the generation of sludge. Adsorption which is
73 the adhesion of ions or molecules onto solid surface has been recognized as efficient method of

74 heavy metals removal from contaminated water since it is cheap and eco-friendly (Gavrilescu *et*
75 *al.*, 2004; Pintilie *et al.*, 2007). The most commonly used adsorbent in the adsorption process is
76 activated carbon, but its soaring cost of fabrication often limits its application (Ho *et al.*, 2004).
77 Thus, the search for various adsorbents with excellent adsorbent properties had been the focus of
78 some researchers in the last decades. Several adsorbents such as bone meal derived apatite
79 (Ofudje *et al.*, 2020), olive cake (Doyurum and Celik, 2006), black gram husk (Saeed *et al.*,
80 2005), kraft lignin (Mohan *et al.*, 2006), tea-industry waste (Cay *et al.*, 2004), bagasse derived
81 activated carbon (Mohan and Singh, 2002) and activated carbon from Filtrasorb (Kappor *et al.*,
82 1999) have been reported for their ability to eradicate cadmium ions in polluted waste water. The
83 advantage of using agricultural byproducts as adsorbents is that they are less expensive to
84 produce and renewable. To this end, this current study presents the sorption of cadmium from
85 aqueous solution by means of renewable and cheaper precursor agriculture by-products from
86 orange peel (OP). The adsorbent was characterized using scanning electron microscope (SEM)
87 and Fourier transform infrared (FT-IR). The roles of initial concentration of adsorbates, contact
88 time, pH, adsorbent dosage and regeneration study were investigated. The Langmuir, Freundlich
89 and Dubinin–Radushkevich models were used to explained the equilibrium isotherm, while
90 Pseudo-first order, Pseudo-second order, Elovich and intraparticle diffusion kinetic models were
91 employed to interpret the kinetic data.

92 **MATERIALS AND METHODS**

93 **Adsorbent Preparation**

94 Orange peel (OP) samples were gathered from Osiele market in Abeokuta area of Ogun State,
95 Nigeria and were rinsed with distilled water, after which they were air dried and later oven dried

96 at 80 °C for 12 hours. Samples were further ground into fine powder, sieved with 0.5 mm sieve.
97 and stored in a container which is air tight for further analysis.

98 **Characterization of the Prepared Adsorbent**

99 Scanning electron microscope (Hitachi, Japan, S-3000H) which is made up of energy dispersive
100 X-ray (EDX) was make used to assessed the elemental composition of BMDA. Fourier transform
101 infrared (FT-IR) spectra were performed from 400 to 4000 cm^{-1} with TENSOR 27 spectrometer
102 (Bruker, Germany). The crystallography of orange peel powder was investigated by Bruker D8
103 Advance X-ray Diffractometer with Cu $K\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation in the 2θ range from 10 to
104 90° .

105 **Preparation of Adsorbate Solutions**

106 Solution of 1000 mg/L of Cd(II) ion was made by weighing 0.4400 g of the $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and
107 dissolved in distilled water using a 250 mL standard flask and made to mark. Various
108 concentrations of cadmium ions (50 - 300 mg/L) working standards were thereafter made from
109 the stock solution in 250 mL standard flasks and made to mark.

110 **Determination of Effect of Agitation Time**

111 The experiment was achieved at a pH of 4.5 with varying contact time of 5, 10, 15, 20, 30, 60
112 and 120 minutes at room temperature. A 0.2 g of adsorbent was introduced into 20 mL each of
113 the metal solution whose concentrations ranged from 50 mg/L to 300 mg/L respectively. The
114 samples were agitated inside a water bath shaker which is temperature controlled at a speed of
115 100 rpm at 30°C . At the expiration of the contact time, suspension of the mixture was filtered,

116 while the remains in the liquid medium was examined using Atomic Absorption
117 Spectrophotometer (AAS) BUCK 211.

118 **Effect of pH on Adsorption Process**

119 0.2 g of the orange peels was dissolved in 25 mL of 300 mg/L of Cd(II) ion solution in the pH
120 range of 2-9. The pH adjustment to desired value was done by the addition of 0.1M HCl and/or
121 0.1M NaOH prior to the addition of the adsorbent. The flask containing the mixture was
122 equilibrated in an Orbital shaker to reach equilibrium at constant agitation speed. The solution
123 was then filtered and Cd(II) concentration left unadsorbed in the solution was investigated using
124 Atomic Absorption Spectrophotometer BUCK 211.

125 **Effect of Temperature**

126 In this study, 0.2 g powdered orange peels was agitated with 25 mL of 100 mg/L of Cd(II) ion
127 solution at pH 4.5 and at different temperatures ranges: 30, 35, 40, 45 and 60 °C. The mixture
128 was shaken constantly with the aid of orbital shaker. The solution was then filtered the liquid
129 portion was determined using Atomic Absorption Spectrophotometer BUCK 211.

130 **Effect of Adsorbent dosage**

131 Impact of dosage of the adsorbent was determined by using various adsorbent dosages from 0.01
132 to 0.10 g and agitating each of them separately with 25 mL of Cd(II) ion solution at best possible
133 conditions. The mixtures were shaken constantly at the agitation time. Then, the solution was
134 separated and the metal contents of the filtrate were measured using Atomic Absorption
135 Spectrophotometer BUCK 211.

136

137 Effect of initial concentration of the Cd(II) Ions on Adsorption

138 Exactly 0.1 g of orange peels powder was treated with 25 mL solution of varying concentration
 139 (25-300 mg/ L) of the pollutant solution at optimal pH 4.5 over 2 hours. The pH was adjusted
 140 using 0.1 M HCl and 0.1 M NaOH. The mixtures were shaken constantly with the aid of an
 141 orbital shaker for 2 hours at 30°C. The solution was then filtered and the filtrate was measured
 142 for Cd(II) ion using Atomic Absorption Spectrophotometer BUCK 211.

143 Kinetic Studies

144 The kinetics investigation of the uptake of Cd(II) ion in an aqueous solution were done using
 145 batch adsorption procedure. In this procedure 0.1 g of sample of OP powder was put in different
 146 200 mL sample tubes and 25 mL of the pollutant was added to each tube. The mixtures were
 147 properly agitated for 2 hours using a water bath shaker to ensure equilibrium was reached. The
 148 content was then separated and the Cd(II) ion remaining in the filtrate was measured using AAS,
 149 BUCK 211. The adsorption capacity (mg/g) and removal efficiency (%) were performed using
 150 the formulas in equations (1) and (2) as indicated below:

$$151 \quad Q_t = \frac{(C_o - C_t)}{m} V \quad (1)$$

$$152 \quad Q_t = \frac{(C_o - C_t)}{C_o} X 100 \quad (2)$$

153 Such that Q_t (mg/g) signify the quantity of Cd(II) ions sorbed at $t = t$; C_0 and C_t (mg/L) are the
154 amount of contaminant present at $t = 0$ and $t = t$ respectively; the mass of the OP used is given as
155 m (g) and the volume of the pollutant used is denoted as V (L).

156 Procedure for Optimization

157 Optimization studies of the adsorption of Cd(II) by the orange peel was performed by preparing
158 three different concentrations (50, 150 and 250 mg/L) of Cd(II) ion solutions, solutions were
159 adjusted to pH values of 1.0, 4.5, and 8.0. Different quantities of adsorbent - 0.1, 0.055 and 0.010
160 g were used. A parallel set of experiments without adsorbent served as blank. The flasks
161 containing the mixture (20 mL) each were set into a thermostated shaker at 30°C and 250 rpm for
162 1 hour. Each of the flasks was then removed at pre-set time, decanted and the concentration of
163 cadmium ions in the filtrate was determined using AAS BUCK 211.

164 RESULTS AND DISCUSSION

165 Characterizations

166 The diverse functional groups present on orange peel surface prior to and after adsorption were
167 analyzed with the aid of FT-IR as shown in Fig. 1. The orange peel demonstrated different
168 functional groups with peak at 3419.82 cm^{-1} identified as O–H vibrations (Adeogun *et al.*,
169 2019), the 2926.74 cm^{-1} peak was recognized as –CH stretching of the alkanes group (Ofudje *et*
170 *al.*, 2017), 1637.43 cm^{-1} peak is that of C=O stretching of carbonyl groups, while the one at
171 1429.33 cm^{-1} is allotted to –CH₃ stretch. The peak noted at 1033.10 cm^{-1} was allotted to the C–
172 O bond of the esters and carboxylic acids groups (Ofudje *et al.*, 2017). Upon the uptake of
173 cadmium ions, shifts in peak positions were observed indicating the possible involvement of

174 these functional groups. For example, peak at 3419.82 cm^{-1} increased to 3442.00 cm^{-1} , while
175 peaks at 2926.74 cm^{-1} and 1637.43 cm^{-1} increased to 2927.77 and 1642.00 cm^{-1} respectively.
176 Similarly, the peaks initially present at 1429.33 and 1033.10 cm^{-1} increased to 1432.21 and
177 1033.26 cm^{-1} respectively. Fig. 2a depicts the SEM image of the OP powder showing the porous
178 structure which could provide more adsorption sites for the cadmium ions uptake. The XRD
179 patterns of the orange peel adsorbent is shown in Fig. 2b with key diffractions at $2\theta = 16.3^\circ$ and
180 22.3° which correspond to the (101) and (200) planes respectively for cellulose thus indicating
181 an amorphous cellulose type I (Ofudje *et al.*, 2017).

182 **Effect of Agitation time and Metal Concentrations**

183 The role of agitation time (0 - 240 min) on the removal of Cd(II) ions was carried out with initial
184 Cd(II) ion concentrations within the range of 50-250 mg/L at a solution pH of 5.5 and is as
185 represented in Fig. 3. The maximum uptake of Cd(II) was at 120 min after which there was no
186 considerable raise in the quantity of the pollutant sorbed. As indicated from the plot, the uptake
187 process happens in two steps with the first one being very quick and was attained at about 47 min
188 with percentage removal of 48.4 % by orange peel adsorbent. The subsequent stage symbolized a
189 progressive reduced adsorption which was achieved at 120 min. The swift early adsorption could
190 be credited to the growth of Cd(II) ions on to the OP surface, owing to the existence of available
191 sites on the OP surface. Nevertheless, with gradual growth of Cd(II) ions on these spots by the
192 cadmium ions, the uptake became sluggish in the second stage, thus leading to reduction in the
193 amount of pollutant adsorbed by the adsorbent (Adeogun *et al.*, 2018, Ofudje *et al.*, 2020).

194 **Effects of pH**

195 Solution pH has been recognized to be a very important factor in the adsorption procedure since
196 it can affect both the chemistry of the adsorbate and adsorbent. The network of charges of the
197 adsorbate and adsorbent relies on the solution pH. With raise in the pH from 2 to 5.5, the
198 sorption capacity of OP rose from 24.62 to 44.42 % as revealed in Fig.4. The highest adsorption
199 was accomplished at a solution pH of 5.5. At smaller pH value, the Cd(II) ion elimination is
200 subdued by web of positive charges of the OP and the rivalry that exist between Cd(II) ions and
201 H^+ in solution. But with elevated pH, the negative charge network on OP increases which is due
202 to the deprotonation of the binding sites. Therefore, the sorption of Cd(II) ions increases
203 (Chunfang *et al.*, 2017, Ofudje *et al.*, 2017).

204 **Effect of Temperature**

205 Fig. 5 demonstrates the dependence of the adsorption of Cd(II) by orange peel on the
206 temperature. The adsorption process was found to be a function of temperature and the highest
207 Cd(II) uptake was achieved at 45 °C. The rise of solution temperature increased the adsorption
208 competence of Cd(II) on OP indicating that the process was endothermic. Increase in
209 temperature increased the rate of the progression of the Cd(II) ions from the solution onto the
210 unoccupied sites of OP and weakened the thickness of the surface layer of OP, thereby
211 enhancing the dispersion resistance of adsorbates to adsorbents (Ofudje *et al.*, 2020).

212 **Effect of Dosage**

213 The percentage removal of Cd(II) on OP significantly increased with the adjustment of OP from
214 0.01 to 0.04 g as depicted in Fig. 6 which showed that adsorption of Cd(II) ion was enhanced as
215 the OP dosage increases. This is owing to more active spots which are accessible for the
216 adsorption of Cd(II) ion due to larger surface area provided by increase in OP concentration. The

217 common patterns of enhanced pollutant adsorption with a raise in sorbent dosage signify the
 218 existence of more binding sites which are available for adsorption.

219 Kinetic studies

220 Plots of Q_t against t were used to determine kinetic values of Pseudo- first-order, Pseudo-
 221 second-order, Elovich and Intraparticle diffusion models which are presented in equations 3 to 6
 222 respectively (Lagergren, 1898; Ho and McKay, 1998; Cheung *et al.*, 2004; Weber and Morris,
 223 1963):

$$224 \quad Q_t = Q_e (1 - e^{-k_1 t}) \quad (3)$$

$$225 \quad Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

$$226 \quad Q_t = \frac{1}{\beta} \ln(\alpha \beta \times t) \quad (5)$$

$$227 \quad Q_t = K_{id} t^{0.5} + C_i \quad (6)$$

228 Given that k_1 (min^{-1}g) and k_2 ($\text{min}^{-1}\text{g}/\text{mg}$) are the rate constants for first- and second-orders
 229 respectively, Q_e (mg/g) signify the quantity of Cd(II) ions adsorbed at equilibrium and Q_t is as
 230 defined previously.

231

232 Test of Kinetic Fitness

233 The best fit among the kinetics models were tested by the sum of error squares (SSE, %) given
 234 by (Adeogun *et al.*, 2013; Ofudje *et al.*, 2017) :

$$235 \quad \% \text{ SSE} = \sqrt{\frac{((Q_{(\text{exp})} - Q_{(\text{Cal})}) / Q_{\text{exp}})^2}{N - 1}} \times 100 \quad (7)$$

236 Such that N represents the data points of number.

237 The estimated values of Q_e , k_1 and k_2 were calculated from the non-linear plots of Q_t against t
 238 in Fig.7 are as presented in Table 1. The R^2 values obtained from the Pseudo-first order equation
 239 ranged from 0.947 to 0.990, whilst that of the second-order equation ranged from 0.953 to 0.993

240 with the Pseudo-second-order showing better values. However, a close inspection at the values
241 of $Q_{e_{exp}}$ and $Q_{e_{cal}}$ of the second-order showed greater differences and this suggested that the
242 second-order equation cannot be useful to describe the uptake process. On the other hand, careful
243 inspection of values of the $Q_{e_{cal}}$ from the first-order model correspond well with the $Q_{e_{exp}}$; which
244 indicated that the Pseudo-first-order model can be used to explain the whole adsorption process
245 of Cd(II) ion onto the surface of OP which is known as physisorption. Investigation of sum of
246 error squares (SSE, %) further affirm suitability with the Pseudo-first-order model when
247 compared with that of second-order model. The rate constant values from the Pseudo-first-order
248 model range from 0.031 to 0.043 min^{-1} . From the Elovich model, α represents the initial rate of
249 adsorption which is measured in mg/g min , while the desorption constant in g/mg is given as β
250 which were derived from the plots of Q_t against t from least square fit method as shown in Fig.
251 7c. Also, K_{id} stands for the intra-particle diffusion rate constant measured in $\text{mgg}^{-1}\text{mins}^{-0.5}$ and C_i
252 stands for the degree of surface thickness. The values of R^2 as obtained from the intraparticle
253 diffusion model are in the range of 0.945 to 0.986 thus, suggesting the applicability of this model
254 in describing the adsorption pattern of the biomass. The uptake process of cadmium ions can be
255 categories into three steps: (i) film mass transfer, (ii) intraparticle diffusion, and (iii) chemical
256 reaction on adsorbent (Ofudje *et al.*, 2017). The preliminary rapid uptake of Cd (II) ion by OP is
257 as a result of the abundant presence of adsorptive sites, greater outer diffusion rate of Cd(II) ions
258 couple with small diameter of Cd(II) ions. However, reduction in adsorption was due to the
259 transfer of Cd(II) ions from external diffusion to internal, while saturated adsorption is as a result
260 of the repulsion between pollutant and sorbent which hindered the activities of the remaining
261 active sites.

262 **Equilibrium Studies**

263 To investigate the equilibrium behaviour of orange peel powder, Langmuir, Dubinin–
 264 Radushkevich (D-R), and Freundlich isotherm were utilized. Langmuir isotherm assumed that
 265 the adsorption energy is the same irrespective of the amount of adsorbed material on the
 266 adsorbent active spots which can be described by the relationship in equation 8 (Langmuir,
 267 1918; Dehghani *et al.*, 2015 and Morovat *et al.*, 2016).

$$268 \quad Q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (8)$$

269 with Q_{\max} standing for the maximum monolayer adsorption capacity (mg/g), while b (L/mg)
 270 denotes the adsorption energy. The Langmuir separation factor (R_L) can be expressed as:

$$271 \quad R_L = \frac{1}{(1 + b C_o)} \quad (9)$$

272 Such that C_o (mg L⁻¹) gives the adsorbate concentration and when the values of R_L lies between 0
 273 and 1, it implies favourable adsorption, if $R_L > 1$, it indicates unfavourable adsorption and if $R_L =$
 274 0, it means irreversible process.

275 Freundlich isotherm described a multisite or multilayer with a heterogeneous surface and is
 276 given according to the equation 10 below (Freundlich, 1906):

$$277 \quad Q_{eq} = K_F C_e^{1/n} \quad (10)$$

278 Given that K_F (mg/g)(mg/L)^{-1/2} the sorption capacity and n is the intensity of adsorption of the
 279 adsorbent respectively. The Dubinin-Radushkevich (D-R) adsorption isotherm is applicable at
 280 low concentration range of adsorbate which could be useful in providing explanations regarding
 281 homogeneous and heterogeneous adsorption surfaces. The non-linear representation of the D–R
 282 equation is given as:

$$283 \quad Q_e = Q_m e^{-\beta \varepsilon^2} \quad (11)$$

284 With Q_m representing the saturation adsorption capacity of the OP, value of β stands for the
 285 adsorption free energy and ε is the potential for Polanyi and can be expressed as:

$$286 \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

287 The ideal molar gas constant is given as R (8.31 J/mol K) and T is temperature (K). Value of the
 288 mean sorption energy, E (kJ/mol), could be estimated from β parameter as thus:

$$289 \quad E = \frac{1}{\sqrt{2\beta}} \quad (13)$$

290 Values of E (kJ/mol) could be used to predict the mechanism of adsorption. For instance, when E
 291 values lie between 8 and 16 kJ/mol, it is an ion-exchange process, but values of E less than 8
 292 kJ/mol suggests physical adsorption process while values of E greater than 16 kJ/mol, imply that
 293 the adsorption process is subjugated by particle diffusion. The plots of the isotherms are as
 294 shown in Fig. 8, while their values are as given in Table 2. The values of R^2 gotten from
 295 Langmuir, Freundlich and D-R isotherms for Cd(II) ions are 0.994, 0.996 and 0.981 respectively,
 296 thus suggesting that the three isothermal models could be employed to describe the equilibrium
 297 adsorption data, particularly the Langmuir and Freundlich models. The maximum adsorption
 298 capacity Q_m and K_F obtained for Cd(II) ions uptake are 27.916 (mg g^{-1}) and 1.431 ($\text{mg/g})(\text{mg/L})^{-1/2}$
 299 $^{1/2}$ in that order. The n values represent the distribution energy of adsorption site. Since $n > 1$, it
 300 indicates feasible adsorption, with greater heterogeneous adsorption site and energy distribution.
 301 Value of R_L obtained is < 1 , which implies that the adsorption was favourable. Dubinin–
 302 Radushkevich (D-R) parameter, E, was found to be 0.068 kJmol^{-1} and since the value of E is
 303 smaller than 8 kJ mol^{-1} , the adsorption mechanism is physical in nature. Table 3 indicates the
 304 potentials of various adsorbents for cadmium ion adsorption compared with orange peel powder

305 from this present study. The result demonstrates better adsorption capacity of orange peel
306 adsorbent compared to tea industry waste and olive cake.

307 **Thermodynamics Studies**

308 The thermodynamic investigation of the adsorption of cadmium onto orange peel was evaluated
309 using the relations:

$$310 \quad \Delta G^\circ = -RT \ln K_d \quad (14)$$

$$311 \quad \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

312 With R standing for the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) and T is the absolute
313 temperature in Kelvin. The free energy change is given as ΔG° , enthalpy change is ΔH° and the
314 entropy change as ΔS°). The plots of $\ln K_d$ versus $1/T$ should give a slope of $\Delta H^\circ/R$ with an
315 intercept of $\Delta S^\circ/R$ as shown in Fig. 9 and the evaluated parameters are as presented in Table 4.
316 Positive value of enthalpy change affirmed the adsorption process to be endothermic, which
317 support the claim early that the process of adsorption is physical in nature. Furthermore, the
318 negative value of the entropy change showed that the degree of randomness decreased as the
319 temperature increased and shows a decreased disorderliness at the solid/solution interface.

320 **Optimization Studies**

321 The mutual relationship of pH and adsorbent dosage on the elimination of Cd by orange peel is
322 represented as contour and 3D plots in Fig. 10a and it clearly depicts that the uptake of Cd(II) by
323 orange peel depends on the solution pH, which was observed to be increasing (till pH of 5.0) and
324 thus optimum adsorption took place at pH 5.5. According to Dehghani *et al.* (2016), decrease in
325 Cd(II) sorption was notable as the solution pH was adjusted from 5.5 to 8. The adsorbent dosage

326 also has a synergistic effect on the percentage removal. The joint effects of sorbent dosage as
327 well as that of Cd(II) ion concentration on the efficiency of adsorption behaviour of OP in the
328 uptake of Cd is presented in Fig.10b . The removal efficiency rose with the sorbent dosage from
329 0.02 to 0.10 g. With greater sorbent dosage, more binding spots become accessible to the Cd(II)
330 on the surface of the sorbent material, which leads to greater removal capability. It was noted
331 optimum removal efficiency of 60 % was accomplished at 0.10 g of the adsorbent dosage. In
332 general, greater sorbent dosage and lesser Cd(II) ion concentration enhanced the uptake of Cd
333 (II) ions (Dehghani *et al.*, 2016). The impact of solution pH on the uptake of Cd(II) ion was also
334 studied in the pH range of 1-8 as presented in Fig.10c. The results showed that as the pH
335 decreases the concentration of Cd(II) ion adsorbed increases.

336 **Conclusion**

337 This study examined the potentials of waste agricultural products of orange peel as less-
338 expensive and environmentally benign adsorbent in the subtraction of cadmium ions from
339 aqueous solution under diverse experimental circumstances. The result from the equilibrium
340 study gave the adsorption capacity of 27.916 mg g⁻¹ at 318 K, while the three isotherm models
341 tested conform well with the contaminant experimental data, although Langmuir demonstrated a
342 better fitting. The kinetic data aligned perfectly with the Pseudo-first-order equation.
343 Thermodynamic analysis showed that the adsorption process was not spontaneous and
344 endothermic in nature and this is an indication of good economic value. Thus, orange peel could
345 be a useful adsorbent for uptake of cadmium ions in contaminated environment.

346 **Abbreviations**

347 AAS: Atomic Absorption Spectrophotometer; a_T : Tempkin constants relating to binding constant
348 (Lmg⁻¹) ; b : Langmuir equilibrium constant (L mg⁻¹); b_T : heat of adsorption; β : Mean free

349 energy of adsorption; C_e : equilibrium concentrations; C_o : initial concentrations; C_i : degree of
 350 surface thickness; E : mean free energy (kJ mol^{-1}); EDX: Energy dispersive X-ray analysis; D-R:
 351 Dubinin–Radushkevich; FT-IR: Fourier-transform infrared spectroscopy; K_F : Freundlich
 352 adsorption capacity; K_{id} : intra-particle diffusion rate constant measured in $\text{mgg}^{-1}\text{mins}^{-0.5}$; K_d :
 353 equilibrium constant; m : adsorbent mass (g); n : adsorbent intensity; Q_e : amount of adsorbate
 354 adsorbed in mg/g ; Q_{max} : maximum amount of solute adsorbed; k_1 : Adsorption rate constant
 355 (min^{-1}) for a Pseudo first-order; k_2 : Rate constant of Pseudo-second-order ($\text{g mg}^{-1} \text{min}^{-1}$); ϵ :
 356 Polanyi potential; OP: orange peel; N : data points of number; R : molar gas constant (8.314 J
 357 $\text{mol}^{-1} \text{ K}^{-1}$); R^2 : Correlation coefficient; R_L : Separation factor; SEM: Scanning electron
 358 microscope; SSE: Sum of square error function; T : Temperature (K); V : volume (L) of the
 359 pollutant taken; XRD: X-ray diffractometer; ΔS° : Entropy change, ΔH° : Enthalpy change; ΔG° :
 360 Free energy change.

361 **Ethics approval and consent to participate**

362 Not applicable

363 **Consent for publication**

364 Not applicable

365 **Availability of data and materials**

366 Not applicable

367 **Competing interests**

368 All authors do declare that there are no competing interests.

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373 All authors have equal contribution to this research work. All authors read and approved the final
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Figure Captures

473 **Fig.1.** FT-IR spectra of OP (a) before and (b) after adsorption of Cd (II) ions

474 **Fig. 2** (a) SEM image and (b) XRD of orange peel adsorbent

475 **Fig.3:** Graphs of agitation time and pollutant concentrations on adsorption of Cd(II) at pH =5.5;
476 sorbent dosage of 0.04 g/L; temperature 45 °C).

477 **Fig.4:** Effects of pH on the uptake of Cd(II), (initial Cd(II) ions concentration = 240 mg/L;
478 adsorbent dosage of 0.04 g/L; temperature 45 °C; agitation time = 120 min).

479 **Fig.5:** Effects of temperature on the uptake of Cd(II) ions, (initial contaminant concentration =
480 240 mg/L; adsorbent dosage of 0.04 g/L; pH = 5.5; agitation time = 120 min).

481 **Fig.6:** Effects of dosage on adsorption of Cd(II), (initial pollutant concentration = 240 mg/L;
482 temperature = 45 °C; pH = 5.5; agitation time = 120 min).

483 **Fig. 7:** Graphs of Q_t against t for (a) Pseudo-first-order, (b) Pseudo-second-order, (c) Elovich
484 and (d) intraparticle kinetic models for the adsorption of cadmium ions at initial metal
485 concentration of 250 mg/L, pH of 5.5 and temperature of 50 °C by orange peel powder.

486 **Fig. 8:** Plots of Q_e versus C_e for Langmuir, Freundlich and D-R adsorption isotherms for the
487 adsorption of cadmium(II) by OP at initial metal concentration of 250 mg/L, pH of 5.5 and
488 temperature of 50 °C.

489 **Fig. 9:** Plot of $\ln K$ against $1/T$ for the adsorption of cadmium by OP

490 **Fig. 10:** 3D plot to show effect of (a) pH and sorbent dosage, (b) sorbent dosage and Cd(II) ion
491 concentration and (c) pH and Cd(II) ion concentration on the percentage adsorption of Cd(II)
492 ions by orange peel.

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495 **Table Capture**

496 **Table 1:** Kinetic Data Values for the Adsorption of Cadmium by OP

497 **Table 2:** Isotherm Parameters of cadmium Adsorption on OP

498 **Table 3:** Comparable Adsorption Capacities of other Adsorbents with Orange Peel

499 **Table 4:** Thermodynamics values for the adsorption of Cd(II) ion

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