



Waste Orange Peel Adsorbent for Heavy Metal Removal from Water

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ABSTRACT

Batch adsorption process was employed to remove copper(II) and cadmium(II) ions from contaminated water using dried orange peel powder as a cellulosic adsorbent, which supports circular economy and sustainability. Metal ion concentrations were determined using flame atomic absorption spectroscopy (FAAS). Effects of pH, sorbate-sorbent contact time, metal ion concentration and adsorbent dose on the removal efficiency of the metal ions were investigated. The adsorption equilibrium was reached at 120 and 150 minutes for Cu(II) ions and Cd(II) ions, respectively. At optimized pH and biosorbent load, 10 mg L⁻¹ of Cu(II) and Cd(II) ions could be removed to the extent 96.9% and 98.1%, respectively, within 2 hrs. However, the percentage removal of metal ions decreased with increasing their initial concentrations. The observed adsorption data was also interpreted in terms of Langmuir and Freundlich adsorption isotherm models. The calculated equilibrium data fitted more adequately with Freundlich model (higher correlation coefficient, R²) than Langmuir model, indicating heterogeneity of adsorption sites due to different functional groups in cellulose. Cd(II) ions showed less binding affinity and less desorption than Cu(II) ions. The maximum adsorption capacity (q_{max}) of dried orange peel were 2.78 mg/g and 2.57 mg/g for copper(II) and cadmium(II) ions, respectively.

Keywords: Adsorption, waste biomass, atomic absorption spectroscopy, heavy metal, cellulose, water pollutant.

INTRODUCTION

Heavy metals, such as copper (Cu), chromium (Cr), lead (Pb), mercury (Hg), arsenic (As) and cadmium (Cd), are major toxic pollutants existent in industrial wastewater and also constitute common groundwater contaminants (Jak et al., 1996; Stylianou et al., 2007). Recently, some researchers (Ali et al., 2019) have presented a comprehensive review of the environmental chemistry and ecotoxicology of hazardous heavy metals and metalloids. Chemical precipitation, membrane filtration, ion exchange liquid extraction and electro-analysis methods are not suitable for implementation at commercial scale to remove heavy metals from contaminated water, due to their high cost and low feasibility. In contrast, the adsorption technique is much more advantageous for removal of heavy metals because of its higher efficiency and low cost. However, since the conventional adsorbents such as granular and powdered activated carbon are not economically viable and technically efficient (Akeson et al., 2008), the recent focus has been on using nature based sustainable minerals and agricultural wastes (Dey, 2007; Dey, 2014) as potential sorbents for the removal of heavy metals from water.

Earlier, numerous low cost and effective sorbents, such as fly ash (Ricou-Hoeffler et al., 2001; Dash et al., 2017), dendrimers (Zhang, 2014), lignin (Li & Ge, 2018), rice husk (Vieira et

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al., 2012), peat (Ho & McKay, 2000), microbial biomass (Ahluwalia & Goyal, 2007) and agricultural byproducts (Jaramillo et al., 2009) have been used for the removal of heavy metals from wastewater. Researchers (Czikkely et al., 2018) have reviewed heavy metal adsorption processes by several organic matters from wastewater. Agro-based waste material can also be used as inexpensive unconventional sorbents for the removal of heavy metal pollutants from the contaminated water (Li & Ge, 2018; Feng et al., 2009; Yuvaraja et al., 2012; Saravanan & Ravikumar, 2015; Wang et al., 2017). Cellulose is the most abundant organic polymer found in agricultural waste. Cellulose is a long-chain polysaccharide with several D-glucopyranose units linked by β -1,4-glycosidic bonds. Cellulosic microfibrils (Dey, 2013) can be obtained by alkaline pre-treatment of agricultural waste, which can be utilized for water treatment (Dey, 2012). The corresponding author (Dey, 2012) has reviewed the effects of nano-size, pH, competing species, temperature, pollutant concentration, contact time and adsorbent dose on heavy metal removal efficiency using magnetic and cellulosic nanomaterials.

Copper is widely used in heat exchangers, motors, plumbing fittings, roofing, chemical and marine equipment, cooking utensils, wood preservatives, anti-fouling agents, paints, electronic appliances and as a trace nutrient in livestock feeds. It enters our environment through coal-fired power stations, metal production, waste incinerators, sewage treatment, agricultural chemicals, earth's crust and cigarette smoke. Copper(II) at lower concentrations is one of essential trace nutrients for plants and animals and functions as bacteriostatic, fungicide, and wood preservative. However, at higher concentrations in air, water and soil, Cu(II) ions become poisonous to organisms including human beings, animals, shellfish and plants. Intake of over dosed copper by humans may cause to severe mucosal and gastrointestinal irritation, hepatic and renal damage, widespread capillary and liver damage, and central nervous problems (Antunes et al., 2003; Larous et al., 2005). Excess copper in soils is toxic to some microorganisms, disrupting nutrient-cycle and inhibiting the mineralization of essential nutrients such as nitrogen and phosphorus.

Cadmium, another toxic heavy metal, enters our environment through various sources such as volcanic activity, effluents from mining, alloys, electroplating, smelting, paint and pigments industries, nickel-cadmium battery wastes, and fertilizers (Iqbal & Edyvean, 2005). Cd (II) ions, if present in drinking water or food material, are hazardous to human as well as animal health (Godt et al., 2006). These can cause damage to kidney, renal dysfunction, bone diseases and liver damage (Iqbal et al., 2007).

Therefore, the removal and recovery of toxic heavy metal ions such as Cu(II) and Cd(II) from contaminated environment is of great importance. Fruit peels are a major source of cellulose, which can offer an effective solution to this issue. For example orange peel, due to its natural abundance, waste resources and minimal processing, could be a potential low-cost adsorbent for water pollutants, hence supporting the principles of circular economy and sustainability. In the present study, dried orange peel abundantly available from soft drink industries as a waste material, has been used as the sorbent for the removal of Cu(II) and Cd(II) ions from their aqueous solutions. Effects of parameters such as pH, sorbent load, sorbate-sorbent contact time, metal ion initial concentration to achieve highest efficiency of the sorbent powder for metal ions removal, have been investigated along with cellulosic adsorption mechanism.

MATERIAL & METHODS

Copper sulphate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MW: 249.68 $\text{g}\cdot\text{mol}^{-1}$], cadmium sulphate [$\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, MW: 769.55 $\text{g}\cdot\text{mol}^{-1}$], ethanol [$\text{C}_2\text{H}_5\text{OH}$, MW: 46.07 $\text{g}\cdot\text{mol}^{-1}$], hydrochloric acid [HCl , MW: 36.46 $\text{g}\cdot\text{mol}^{-1}$] and sodium hydroxide (NaOH , MW: 39.99 $\text{g}\cdot\text{mol}^{-1}$) from FLUKA were of analytical

grade and deionized water was used as a solvent.

The orange peel collected from local sources was thoroughly washed with deionized water and then air-dried in an oven at 70°C for 24 hrs. The dry orange peels were ground to fine powder, sieved using 1 mm mesh and preserved in an air tight bottle before further use. The dried orange peel powder (50 g) thus prepared, was soaked in 250 mL ethanol and treated with 250 mL of 1% NaOH solution at room temperature for 24h. Alkaline pre-treatment is an excellent method to remove chlorophyll pigments and other interfering substances of relatively low molecular mass e.g. hemicellulose, lignin, wax and pectin (Brinchi et al., 2013). The resulting mixture was then filtered and the residue was thoroughly washed with de-ionized water and again air-dried at 70°C in an oven for 6 hrs. There are some reports of using chemically modified orange peel as adsorbent, but our aim was to keep the process as simple and natural as possible.

Heavy metal ion solution (100 mL) of known concentration (in mg/L), taken in a 250 mL Erlenmeyer, was mixed with a known amount of the as-prepared orange peel powder. The pH of the mixture was adjusted to the desired level, using 0.1M HCl and 0.1M NaOH, and measured on a pH-meter (MP 220). The mixture was then stirred using a rotary shaker (SO1 Orbital shaker, UK). Five mL each of the reaction mixture, collected at intervals, was filtered using a Whatman No. 1 filter paper and the filtrate was analyzed for metal ion concentration using a flame atomic absorption spectrophotometer (FAAS, Scientific Model: 210VGP) equipped with deuterium background corrector, hollow cathode lamp and standard air-acetylene flame system. Radiation wavelength, lamp current and slit width used in the FAAS were optimized for each analyzed metal. The reagent blanks and samples were aspirated into FAAS consecutively and minimum of three readings were taken. Metal ion concentration contents of samples were determined using their respective pre-constructed standard calibration curves.

Percent removal of the metal ion was obtained using the relation:

$$\% \text{ Removal} = [(c_o - c_e)/c_o] \times 100 \quad (1)$$

where, c_o = the initial concentration (mg/L) of metal ion and c_e = metal ion concentration (mg/L) at sorbate-sorbent equilibrium stage.

At the equilibrium stage, the aqueous phase concentration of adsorbate is measured and the adsorption capacity (q_e) is given by the expression:

$$q_e = v/w (c_o - c_e) \quad (2)$$

where, q_e = adsorption capacity of adsorbent (mg/g), v = volume of reaction mixture in liters and w = weight of the sorbent used in gram, and c_o and c_e are initial and equilibrium concentrations of adsorbate, respectively, in mg/L.

RESULTS AND DISCUSSION

Effects of various parameters on the percent adsorption of Cu(II) and Cd(II) on the adsorbent are described below.

Plots of % adsorption of Cu(II) ions and Cd(II) ions as a function of adsorbate-adsorbent contact time at fixed adsorbent dose (20 g/L), adsorbate concentration (50 mg/L) and agitation speed (180 rpm) are shown in Figure 1. Initially, the adsorption rate increased with time, however, an adsorbate-adsorbent equilibrium was reached at 120 and 150 minutes for Cu(II)

ions and Cd(II) ions, respectively. The steep increase in adsorption at the initial contact time can be attributed to a large number of surface sites available for adsorption, however as the adsorbent sites get saturated by adsorbate, an equilibrium stage is reached.

Plots of percent adsorption as a function of pH for Cu(II) ions and Cd(II) ions using initial metal ions concentration (c_0) of 50 mg/L, adsorbent dose of 20g/L, adsorbate-adsorbent contact time of 150 min and agitation speed of 180 rpm, are presented in Figure 2. To achieve the maximum adsorption efficiency for Cu(II) and Cd(II), the optimum pH for these systems were found to be 4 and 6, respectively. A research group (Nascimento et al., 2019) has measured the point of zero charge (PZC) of orange peel by salt addition method and found it to be 3.5. This means that in a solution with pH less than PZC, the orange peel surface is supposed to be positively charged, whereas at a pH above PZC orange peel surface is negatively charged, favoring adsorption of positively charged metal ions, which supports our observation.

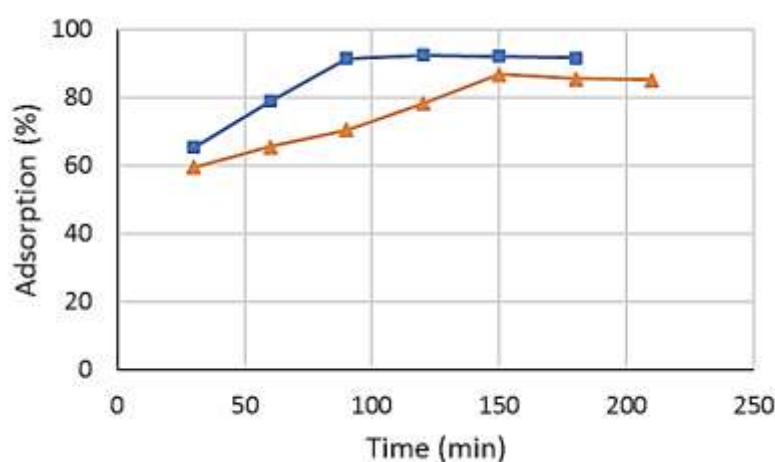


Fig 1: Plots of percent adsorption as a function of sorbate-sorbent contact time. Square: Cu(II) ion, Triangle: Cd(II) ion [adsorbate initial concentration (c_0): 50 mg/L, adsorbent dose: 20 g/L and agitation speed: 180 rpm].

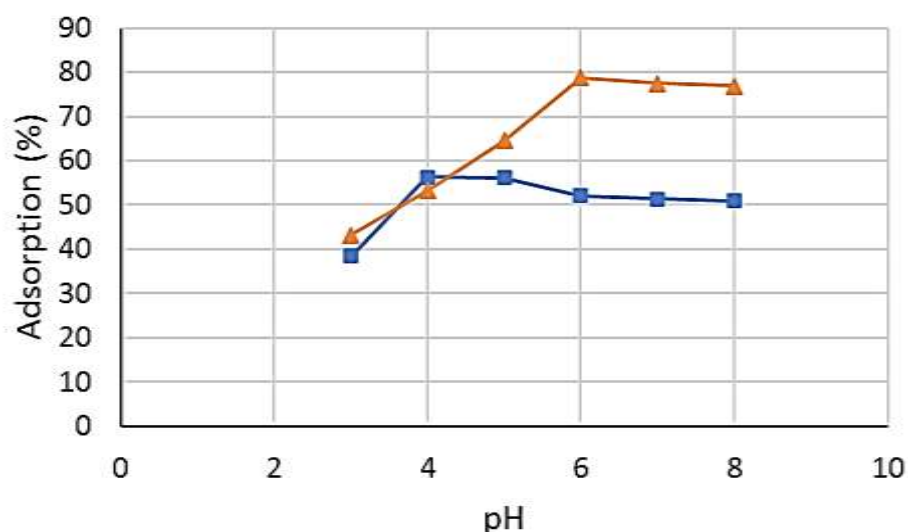


Fig 2: Plots of percent adsorption as a function of pH. Square: Cu(II) ion, Triangle: Cd(II) ion [metal ion initial concentration (c_0): 50 mg/L, adsorbent dose: 20g/L, adsorbate-adsorbent contact time: 150 min and agitation speed: 180 rpm].

In order to minimize the cost of the overall process and also to enhance its efficiency, a knowledge of optimum amount of the adsorbent to be used is essential. Plots of percent ad-

sorption of Cu(II) ions and Cd(II) ions as a function of adsorbent dose at fixed adsorbate initial concentration (50 mg/L), optimum pH [4 for Cu(II) and 6 for Cd(II)], optimum time [120 min for Cu(II) and 150 min for Cd(II)] and agitation speed (180 rpm) are presented in Figure 3. Initially, with increasing adsorbent amount, the adsorption rate of metal ion increases, due to the availability of more active sites for interaction per adsorbate ion (Esposito et al., 2001). However, on further addition of the adsorbent when the adsorbate-adsorbent equilibrium is reached, any further improvement in adsorption rate ceases. The slight increase in adsorption of Cu(II) during this equilibrium stage can be attributed to slow diffusion of some Cu(II) ions through the pores of the adsorption sites, possibly due to smaller size than that of Cd(II). Thus, the optimum adsorbent dose for Cu(II) and Cd(II) ions under the above specified conditions was 25 g/L.

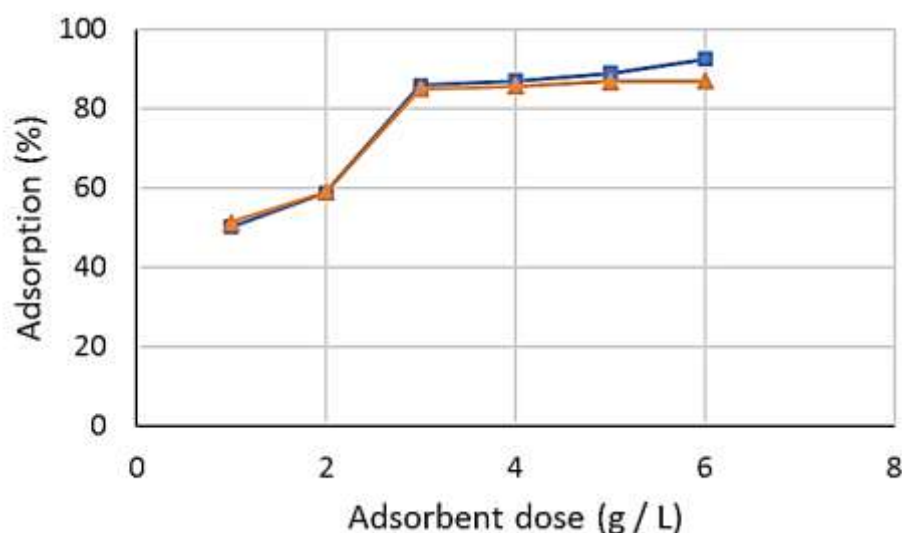


Fig 3: Plots of percent adsorption of studied metal ions as a function of adsorbent dose. Square: Cu(II) ion, Triangle: Cd(II) ion [adsorbate initial concentration: 50 mg/L, optimum pH: 4 for Cu(II) and 6 for Cd(II), optimum time: 120 min for Cu(II) and 150 min for Cd(II), and agitation speed: 180 rpm].

Plots of percent adsorption as a function of initial concentration of studied metal ions using optimum adsorbent dose (25 g/L), pH [3 for Cu(II) ions and 6 for Cd(II) ions] and agitation speed (180 rpm) are presented in Figure 4. Adsorption of heavy metal ions [Cu(II) or Cd(II) ions] with their increasing concentration is lowered throughout the studied metal ion concentration range. It may be due to the availability of fewer adsorbent sites per metal ion for ionic interaction followed by adsorbate-adsorbent complex formation, when the adsorbate concentration is increased at a given adsorbent dose (Yu et al., 2003). It is observed that at optimized pH and biosorbent load, Cu(II) and Cd(II) ions, each with initial concentration 10 mg/L, could be removed to the extent 96.91% and 98.1% respectively, within 2 hrs.

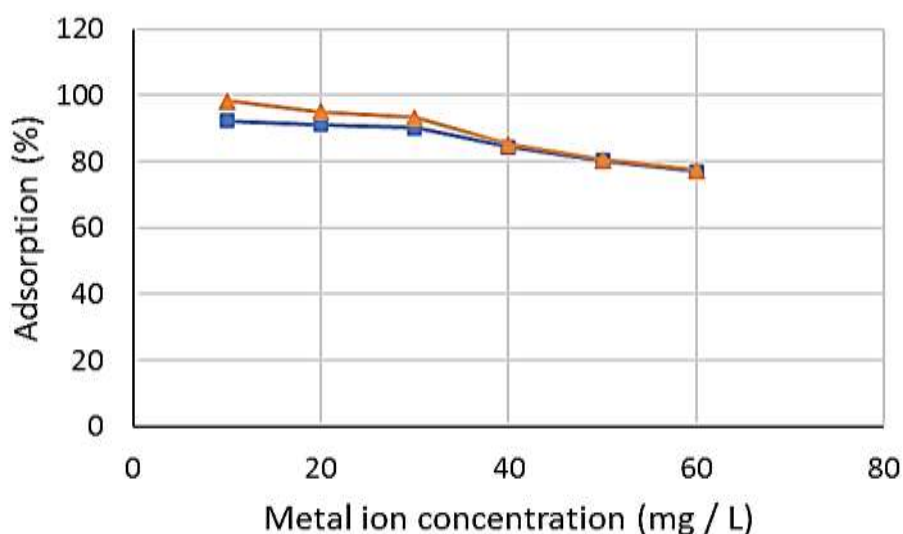


Fig 4: Plots of percent adsorption as a function of initial concentration of metal ion. Square: Cu(II) ion, Triangle: Cd(II) ion [optimum adsorbent dose: 25 g/L, pH: 3 for Cu(II) and 6 for Cd(II), and agitation speed 180 rpm].

An adsorption isotherm may explain the adsorption process and enable determination of the adsorption efficiency of an adsorbent for an adsorbate. There are numerous two-parameter isotherm models e.g. Langmuir, Freundlich, Elovich, Tempkin, Dubnin-Raduskevich (D–R), Harkin-Jura, and BET isotherm that can be employed for equilibrium modeling of adsorption data. The observed data have been interpreted in terms of Langmuir as well as Freundlich adsorption models. The Langmuir model (Langmuir, 1918) assumes uniform energy of adsorption and no transmigration of adsorbate forming a monolayer on the adsorbent surface, whereas the Freundlich isotherm (Freundlich, 1906) is empirical in nature and is widely used for liquid phase adsorption. On the other hand, BET adsorption isotherm assumes multi-layered adsorption of sorbate on the sorbent surface.

The Langmuir isotherm for the adsorption of adsorbate in solution is given by the equation:

$$q_e = q_m \cdot bc_e / (1 + bc_e) \quad (3)$$

where q_e is milligrams of sorbate (here, metal ions) accumulated per gram of the sorbent material (here, orange peel powder); q_m is the maximum specific uptake (mg/g) at equilibrium and ' c_e ' is the sorbate (metal ion) equilibrium concentration in solution; and ' b ' is the ratio of adsorption and desorption rates.

The linear form of Langmuir isotherm is given by the following equation (Langmuir, 1918):

$$c_e/q_e = c_e/q_m + 1/bq_m \quad (4)$$

On plotting c_e/q_e against c_e , a straight line is obtained with slope $1/q_m$ and intercept $1/bq_m$.

Linear plots of c_e/q_e versus c_e , for Cu(II) and Cd(II) ions as adsorbates and orange peel as adsorbent are presented in Figure 5. The slope and intercept of these plots give the values of $1/q_m$ and $1/bq_m$. and thus the parameters ' q_m ' and ' b ' can be obtained and these are given in Table 1. The higher q_m value for Cu(II) (2.78 mg/g) compared to that of Cd(II) (2.57 mg/g)

indicates more adsorption capacity of the studied orange peel powder for the former ion, which is in line with the experimentally observed percent absorption of these ions.

The essential characteristic of the Langmuir isotherm may be expressed in terms of a separation parameter R_L (mg/L), which is defined as:

$$R_L = 1 / (1 + bc_0) \quad (5)$$

The parameter R_L is indicative of the adsorption isotherm's shape and can predict the feasibility of an adsorption process (Juang et al., 1997). The value of separation parameter, R_L , indicates the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The calculated values of R_L for the adsorption of Cu(II) and Cd(II) on the studied adsorbent, as given in Table 1, are 0.338 and 0.238 respectively proving favorable adsorption process.

Table 1: Langmuir and Freundlich constants for the adsorption of Cu(II) and Cd(II) on orange peel powder adsorbent.

Metal ions	Langmuir			Freundlich			
	q_{\max}	b	R^2	R_L	K_f	n	R^2
Cu(II)	2.78	0.196	0.947	0.338	0.78	2.34	0.996
Cd(II)	2.57	0.320	0.971	0.238	0.49	1.83	0.999

q_{\max} = maximum adsorption capacity (mg/g), b = constant related to binding energy, R^2 = correlation coefficient, R_L = separation factor (mg/L), K_f = Freundlich adsorption capacity, n = Freundlich constant related to intensity of adsorption.

The Freundlich adsorption isotherm (Freundlich, 1906) is empirical and assumes multi-layered adsorption of adsorbate on the adsorbent surface. The Freundlich adsorption equation is a widely used mathematical description of adsorption in aqueous system and is expressed as:

$$q_e = K_f (c_e)^{1/n} \quad (6)$$

where, ' c_e ' is the adsorbate equilibrium concentration and ' K_f ' and ' n ' are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Freundlich adsorption equation in logarithmic form can be written as:

$$\text{Log } q_e = \text{Log } K_f + (1/n) \text{Log } c_e \quad (7)$$

The linear plots of $\text{Log } q_e$ versus $\text{Log } c_e$ for Cu(II) and Cd(II) as adsorbates and orange peel powder as adsorbent, are presented in Figure 6. From the slope and intercept of these linear plots the values of the Freundlich parameters ' K_f ' and ' n ' can be easily obtained and these are also included in Table 1. The calculated higher K_f as well as ' n ' values in favor of Cu(II) ions compared to the corresponding values for Cd(II) ions, indicate more adsorption capacity as well as intensity of the former ion which is in agreement with the actually observed percentage adsorption of these ions on the studied orange peel powder.

Homogeneous and equal energy adsorption sites and monolayer adsorption are the basic assumptions associated with Langmuir isotherm, whereas Freundlich isotherm takes into consideration the surface heterogeneity and exponential distribution of active sites and their energies. However, from the correlation coefficients of adsorption isotherm fitting (Table 1, Figures 5 and 6), it is apparent that the observed data fits much better with Freundlich model than

Langmuir model [R^2 values of 0.996 vs. 0.947 for Cu(II) ion and R^2 values of 0.999 vs. 0.971 for Cd(II) ion]. This is because alkali treated dried orange peel surface has porous microstructure and contains a lot of hydroxyl and carbonyl groups present in cellulose and hemicellulose, which has been proven from earlier FTIR study (Xie et al., 2014). Two different slopes in Langmuir isotherm (Figure 5) are an indication of different binding sites present in the system, moreover, a better fit with Freundlich model supports the heterogenous nature of orange peel adsorbent. This is where our findings stand out from the rest of the publications on orange peel adsorbent for heavy metal removal, where the authors have claimed good agreement with both Langmuir and Freundlich models.

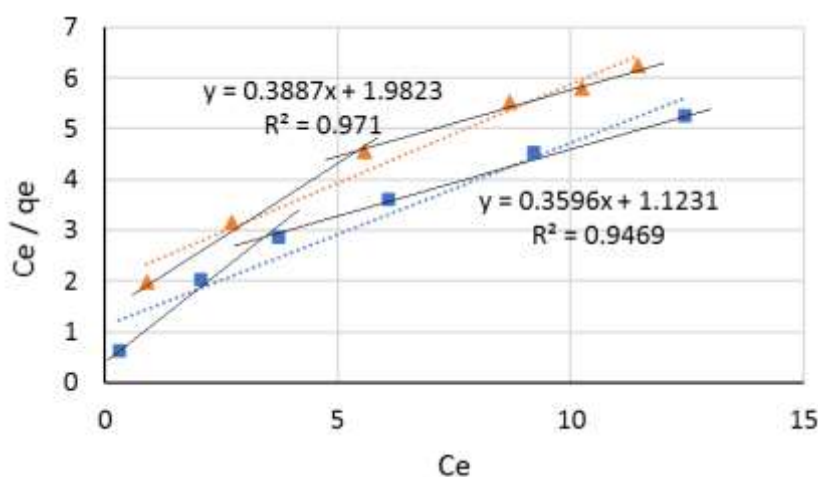


Fig 5: Langmuir adsorption isotherms (plots of c_e/q_e versus c_e). Square: Cu(II) ion, Triangle: Cd(II) ion.

Electrostatic interaction, cation exchange and surface complexation are the main mechanisms operative in this adsorption process. Thermodynamics of surface adsorption can be monitored experimentally (Chatterjee et al., 2001), which can throw some light on spontaneity and endothermic/exothermic nature of the adsorption from changes in free energy and enthalpy, respectively. In particular, isothermal titration calorimetry can determine the thermodynamics of metal ion binding on biopolymer (Karlsen et al., 2010), where different ranges of free energy changes correspond to different binding sites. The higher b value of Langmuir isotherm obtained for Cd(II) ion (0.32) compared to that of Cu(II) ion (0.196), as shown in Table 1, indicates less desorption of Cd(II). On the other hand, the separation parameter R_L is a measure of metal ion affinity of the peel surface and the values of R_L corroborates with that of K_f in Table 1.

It is necessary to compare the equilibrium adsorption capacity values of our study with those obtained from literature. However, in doing so, it should be kept in mind that we have not used any chemically modified biomass adsorbent such as KCl modified orange peel (Cao et al., 2011), citric acid modified orange peel (Li et al., 2007), epichlorohydrin treated rice husk (Kumar & Bandyopadhyay, 2006) etc., activated carbon (Deiana et al., 2009) or biochar (Naeem et al., 2019; Liu et al., 2019) adsorbents derived from biomass, any adsorbent material extracted from biomass such as alginate from red algae (Lucaci et al., 2020), bacterial adsorbent, and presence of EDTA chelating ligand to scavenge metal ions (Dey & Naughton, 2017) or ultrasonics to boost adsorption (Hamdaoui, 2009). So, we will be comparing similar literature reports only.

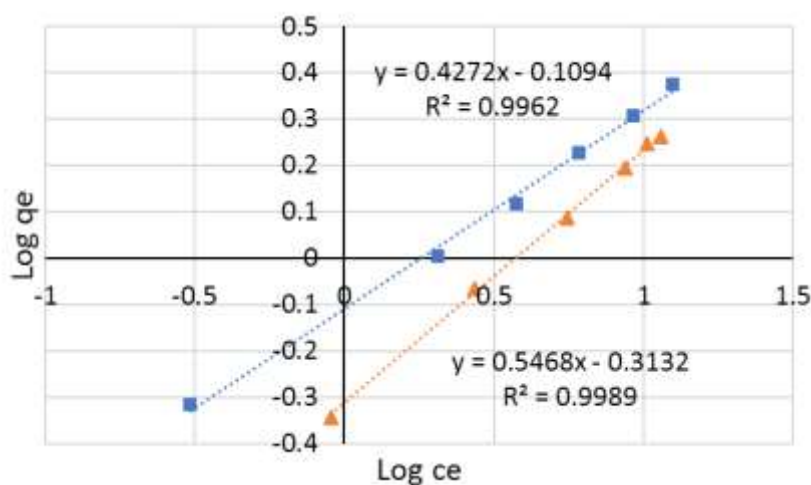


Fig 6: Freundlich adsorption isotherm (plots of $\text{Log } q_e$ versus $\text{Log } c_e$). Square: Cu(II) ion, Triangle: Cd(II) ion.

Table 2: Comparison of Cd(II) adsorption capacity with literature and contributing factors.

Unmodified agricultural biosorbent	Adsorption capacity, q_{\max} (mg/g)	Adsorbent dose (g/L)	Initial adsorbate concentration (mg/L)	Reference
Coconut copra meal	4.92	20	128	Ho and Ofomaja, 2006
Fig leaves (<i>Ficus carcia</i>)	30.31	5	40	Farhan et. al. 2013
Longan hull	4.19	0.5	50	Guo et. al. 2018
Rice husk	41.15	0.2	10	El-Moselhy et. al. 2017
Olive leaves	42.19	0.7	100	Hamdaoui 2009
Cocoa pod husk (<i>Theobroma cacao</i>)	4.42	20	100	Obike et. al. 2018
Green alga (<i>Ulva lactuca</i>)	29.1	10	10	Ghoneim et al. 2014
Pine sawdust	3.47	0.4	60	Liu et. al. 2019
Sawdust	26.73	10	10	Naiya et. al. 2009
Neem bark	25.57	10	10	Naiya et. al. 2009
Eucalyptus bark	14.53	4	100	Ghodbane et. al. 2008
Orange peel	2.57	20	50	Present study

Tables 2 and 3 shows the adsorption capacity, adsorbent dose and initial metal ion concentration of Cd(II) and Cu(II) respectively for a wide range of agricultural bioadsorbents. The adsorption capacity of this present study is on the lower side, which can be explained by the contributing parameters. Initial metal ion concentration (in mg/L) is a key factor related to adsorption capacity. An increase in initial metal ion concentration offers the necessary driving force to overcome the resistance to the mass transfer of metal ion between the aqueous and solid phases (Guo et al., 2018), causing higher adsorption capacity. Apart from solid-liquid ratio, another important factor in adsorption is adsorbent dose (in g/L). With high concentration adsorbent, coagulation of adsorbent particles occur leading to reduction in available functional groups for interaction with metal ions, resulting in lower adsorption capacity (Naseem

et al., 2018). Based on these explanations, if we take a look at Tables 2 and 3, we see most of the researchers have used either higher initial metal ion (adsorbate) concentration or lower biomass (adsorbent) concentration or both, which contributed to their higher adsorption capacity reported in literature.

Table 3: Comparison of Cu(II) adsorption capacity with literature and contributing factors.

Unmodified agricultural biosorbent	Adsorption capacity, q_{\max} (mg/g)	Adsorbent dose (g/L)	Initial adsorbate concentration (mg/L)	Reference
Grape vine bark	43	0.5	100	Haydar et. al. 2020
Fig leaves (<i>Ficus carica</i>)	30.31	0.5	50	Farhan et. al. 2013
Grape stalks	19.9	2	100	Machado et. al. 2003
Sesame husk	10.83	10	30	El-Araby et al. 2017
<i>Vigna radiata</i> husk	11.05	0.1	50	Naseem et. al. 2018
Banana peel	28.56	0.5	125	Afolabi et. al. 2021
Cocoa pod husk (<i>Theobroma cacao</i>)	4.16	20	100	Obike et. al. 2018
Orange peel, alkali treated	1.55	1	15	Annadurai et. al. 2002
Banana peel, alkali treated	2	1	15	Annadurai et. al. 2002
Rice husk	133.34	0.2	10	El-Moselhy et. al. 2017
Jatropha bark	11.54	8	10	Nacke et. al. 2016
Orange peel	2.78	20	50	Present study

CONCLUSION

In order to achieve the maximum removal efficiency of the heavy metal ions Cu(II) and Cd(II) from their aqueous solutions, using low-cost orange peel powder as cellulosic adsorbent, the optimum pH as well as the optimum adsorbent dose should be used. The adsorption equilibrium was reached at 120 and 150 minutes for Cu(II) ions and Cd(II) ions, respectively. These metal ions, with an initial concentration of 10 mg/L, could be removed to the extent of 96.9% and 98.1%, respectively, within 2 hrs. The adsorption data fitted more well with the Freundlich adsorption isotherm rather than the Langmuir one, indicating heterogenous surface. Cd(II) ion showed less binding affinity and less desorption than Cu(II) ion, for orange peel surface. The maximum adsorption capacity (q_{\max}) of dried orange peel were 2.78 mg/g and 2.57 mg/g for copper(II) and cadmium(II) ions, respectively. The use of inexpensive biosorbents can be a viable alternative for the treatment of water against heavy metal pollutants as well as for a waste management strategy.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this

manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCES

- Afolabi, F. O., Musonge, P. and Bakare, B. F. (2021). Bio-sorption of copper and lead ions in single and binary systems onto banana peels. *Cogent Engineering*, 8(1); 1886730.
- Ahluwalia, S. S. and Goyal, D. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, 98(12); 2243-2257.
- Akesson, A., Julin, B. and Wolk, A. (2008). Long-term dietary cadmium intake and postmenopausal endometrial cancer incidence: a population-based prospective cohort study. *Cancer Research*, 68(15); 6435-6441.
- Ali, H., Khan, E. and Ilahi, I. (2019). Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation *Journal of Chemistry*, article ID 6730305, 14 pages. DOI: 10.1155/2019/6730305
- Annadurai, G., Juang, R. S. and Lee, D. J. (2002). Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology*, 47(1); 185-190.
- Antunes, W. M., Luna, A. S., Henriques, C. A. and da Costa, A. C. A. (2003). An evaluation of copper biosorption by a brown seaweed under optimized conditions. *Electronic J. Biotech.*, 6(3); 174-184.
- Brinchi, L., Cotana, F., Fortunati, E. and Kenny, J. M. (2013). Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. *Carbohydrate Polymers*, 94(1); 154-169.
- Cao, Z., He, Y., Sun, L. and Cao, X. (2011). Removal of heavy metal ions from aqueous solutions by adsorption using modified orange peel as adsorbent. *Advanced Materials Research*, 236-238; 237-240.
- Chatterjee, A., Dey, T., Sanyal, S. K. and Moulik, S. P. (2001). Thermodynamics of micelle formation and surface chemical behaviour of p-tert-octylphenoxypolyethylene ether (Triton X-100) in aqueous medium. *Journal of Surface Science and Technology*, 17(1-2); 1-15.
- Czikkely, M., Neubauer, E., Fekete, I., Ymeri, P. and Fogarassy, C. (2018). Review of heavy metal adsorption processes by several organic matters from wastewaters. *Water*, 10(10); 1377-1392.
- Dash, S., Chaudhuri, H., Gupta, R., Udayabhanu, G. and Sarkar, A. (2017). Fabrication and application of low-cost thiol functionalized coal fly ash for selective adsorption of heavy toxic metal ions from water. *Indust. & Engg. Chem. Res.*, 56(6); 1461-1470.
- Deiana, A. C., Sardella, M. F., Silva, H., Amaya, A. and Tancredi, N. (2009). Use of grape stalk, a waste of the viticulture industry, to obtain activated carbon. *J. Hazard. Mater.*, 172(1); 13-19.
- Dey, T. (2007). Properties of vinyl ester resins containing methacrylated fatty acid comonomer: the effect of fatty acid chain length. *Polymer International*, 56(7); 853-859.
- Dey, T. (2012). Magnetic nanoparticles and cellulosic nanofibers to remove arsenic and other heavy metals from water. In: *Nanotechnology for Water Purification*, Universal-Publishers, Florida, pp. 1-28.
- Dey, T. (2013). Cellulosic oleogel as trans-fat substitute: Viscoelastic and structural properties. *LWT - Food Science and Technology*. DOI: 10.1016/j.lwt.2013.07.015
- Dey, T. (2014). Thermal properties of a sustainable cement material: Effect of cure conditions. *Ceramics – Silikáty*, 58(4); 275-281.
- Dey, T. and Naughton, D. (2017). Cheap non-toxic non-corrosive method of glass cleaning evaluated by contact angle, AFM, and SEM-EDX measurements. *Environmental Science and Pollution Research*, 24(15); 13373-13383.

- El-Araby, H. A., Ibrahim, A. M. M. A., Mangood, A. H. and Abdel-Rahman, A. A-H. (2017). Sesame husk as adsorbent for copper(II) ions removal from aqueous solution. *Journal of Geoscience and Environment Protection*, 5(7); 109-152.
- El-Moselhy, K. M., Azzem, M. A., Amer, A. and Al-Prol, A. E. (2017). Adsorption of Cu(II) and Cd(II) from aqueous solution by using rice husk adsorbent. *Phys Chem Ind J.*, 12(2); 109.
- Esposito, A., Pagnanelli, F., Lodi, A., Solisio, C. and Veglio, F. (2001). Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations. *Hydrometallurgy*, 60(2); 129-141.
- Farhan, A. M., Al-Dujaili, A. H. and Awwad, A. M. (2013). Equilibrium and kinetic studies of cadmium(II) and lead(II) ions biosorption onto *Ficus carica* leaves. *International Journal of Industrial Chemistry*, 4; 24.
- Feng, N-C., Guo, X-Y. and Liang, S. (2009). Kinetic and thermodynamic studies on biosorption of Cu(II) by chemically modified orange peel. *Transactions of Nonferrous Metals Society of China*, 19(5); 1365-1370.
- Freundlich, H. M. F. (1906). Uber die adsorption in losungen. *Zeitschrift für Physikalische Chemie*, 57(1); 385-470.
- Ghodbane, I., Nouri, L., Hamdaoui, O. and Chiha, M. (2008). Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark. *J. Hazard. Mater.*, 152(1); 148-158.
- Ghoneim, M. M., El-Desoky, H. S., El-Moselhy, K. L., Amer, A., El-Naga, E. H. A., Mohamedein, L. I. and Al-Prol, A. E. (2014). Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*. *Egyptian Journal of Aquatic Research*, 40(3); 235-242.
- Godt, J., Scheidig, F., Grosse-Siestrup, C., Esche, V., Brandenburg, P., Reich, A. and Gronenberg, D. A. (2006). The toxicity of cadmium and resulting hazards for human health. *J Occup Med Toxicol.*, 1; 22.
- Guo, H., Tang, S., Song, Y. and Nan, J. (2018). Adsorptive removal of Ni²⁺ and Cd²⁺ from wastewater using a green longan hull adsorbent. *Adsorption Science & Technology*, 36(1-2); 762-773.
- Hamdaoui, O. (2009). Removal of cadmium from aqueous medium under ultrasound assistance using olive leaves as sorbent. *Chemical Engineering and Processing*, 48(6); 1157-1166.
- Haydar, S., Farooq, M. U. and Gull, S. (2020). Use of grape vine bark as an effective biosorbent for the removal of heavy metals (copper and lead) from aqueous solutions. *Desalination and Water Treatment*, 183; 307-314.
- Ho, Y. S. and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.*, 34(3); 735-742.
- Ho, Y-S. and Ofomaja, A. E. (2006). Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochemical Engineering Journal*, 30(2); 117-123.
- Iqbal, M. and Edyvean, R. G. J. (2005). Loofa sponge immobilized fungal biosorbent: a robust system for cadmium and other dissolved metal removal from aqueous solution. *Chemosphere*, 61(4); 510-518.
- Iqbal, M., Saeed, A. and Zafar, S. I. (2007). Hybrid biosorbent: an innovative matrix to enhance the biosorption of Cd(II) from aqueous solution. *J. Hazard. Mater.*, 148(1-2); 47-55.
- Jak, R. G., Maas, J. L. and Scholten, M. C. Th. (1996). Evaluation of laboratory derived toxic effect concentrations of a mixture of metals by testing freshwater plankton communities in enclosure. *Water Res.*, 30(5); 1215-1227.
- Jaramillo, J., Gómez-Serrano, V. and Álvarez, P. M. (2009). Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones. *J. Hazard Mater.*, 161(2-3); 670-676.
- Juang, R. S., Wu, F. C. and Tseng, R. L. (1997). The ability of activated clay for the adsorption of dyes from aqueous solutions. *Environmental Technology*, 18(5); 525-531.
- Karlsen, V., Heggset, E. B. and Sorlie, M. (2010). The use of isothermal titration calorimetry to determine the thermodynamics of metal ion binding to low-cost sorbents. *Thermochimica Acta*, 501(1-2); 119-121.
- Kumar, U. and Bandyopadhyay, M. (2006). Sorption of cadmium from aqueous solutions using pre-treated rice husk. *Bioresour. Technol.*, 97(1); 104-109.

- Langmuir, I. (1918). The adsorption of gases on plane surface of glass, mica and platinum. *J. Amer. Chem. Soc.*, 40(9); 1361-1403.
- Larous, S., Meniai, A-H. and Bencheikh Lehocine, M. (2005). Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination*, 185(1-3); 483-490.
- Li, X., Tang, Y., Xuan, Z., Liu, Y. and Luo, F. (2007). Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution. *Sep. Puri. Technol.*, 55(1); 69–75.
- Li, Z. and Ge, Y. (2018). Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. *ACS Sustainable Chemistry & Engineering*, 6(5); 7181-7192.
- Liu, X., Xu, X., Dong, X. and Park, J. (2019). Adsorption characteristics of cadmium ions from aqueous solution onto pine sawdust biomass and biochar. *BioResources*, 14(2); 4270-4283.
- Lucaci, A. R., Bulgariu, D., Popescu, M-C. and Bulgariu, L. (2020). Adsorption of Cu(II) ions on adsorbent materials obtained from marine red algae *Callithamnion corymbosum* sp. *Water*, 12(2); 372.
- Machado, R., Santos, C., Correia, M. J. N. and Carvalho, J. R. (2003). Biosorption of copper by grape stalks and pine bark biomasses. *European Journal of Mineral Processing and Environmental Protection*, 3(1); 108-118.
- Nacke, H., Goncalves Jr, A. C., Campagnolo, M. A., Coelho, G. F., Schwantes, D., dos Santos, M. G., Briesch Jr, D. L. and Zimmermann, J. (2016). Adsorption of Cu (II) and Zn (II) from water by *Jatropha curcas* L. as biosorbent. *Open Chem.*, 14(1); 103-117.
- Naeem, M. A., Imran, M., Amjad, M., Abbas, G., Tahir, M., Murtaza, B., Zakir, A., Shahid, M., Bulgariu, L. and Ahmad, I. (2019). Batch and column scale removal of cadmium from water using raw and acid activated wheat straw biochar. *Water*, 11(7); 1438.
- Naiya, T. K., Chowdhury, P., Bhattacharya, A. K. and Das, S. K. (2009). Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. *Chemical Engineering Journal*, 148(1); 68-79.
- Naseem, K., Huma, R., Shahbaz, A., Jamal, J., Rehman, M. Z. U., Sharif, A., Ahmed, E., Begum, R., Irfan, A., Al-Sehemi, A. G. and Farooqi, Z. H. (2018). Extraction of heavy metals from aqueous medium by husk biomass: adsorption isotherm, kinetic and thermodynamic study. *Zeitschrift für Physikalische Chemie*, 233(2); 201-223.
- do Nascimento, K. K. R., Vieira, F. F., de Almeida, M. M., da S Buriti, J., Barros, A. J. M. and de Oliveira, R. J. (2019). Use of sweet ‘Pêra’ peel as an adsorbent in the treatment of textile effluents. *R. Bras. Eng. Agríc. Ambiental*, 23(9); 716-722.
- Obike, A. I., Igwe, J. C., Emeruwa, C. N. and Uwakwe, K. J. (2018). Equilibrium and kinetic studies of Cu (II), Cd (II), Pb (II) and Fe (II) adsorption from aqueous solution using cocoa (*Theobroma cacao*) pod husk. *J. Appl. Sci. Environ. Manage.*, 22(2); 182-190.
- Ricou-Hoeffler, P., Lecuyer, I. and Le Cloirec, P. (2001). Experimental design methodology applied to adsorption of metallic ions onto fly ash. *Water Research*, 35(4); 965-976.
- Saravanan, R. and Ravikumar, L. (2015). The use of new chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. *Journal of Water Resource and Protection*, 7(6); 530-545.
- Stylianou, M. A., Hadjiconstantinou, M. P., Inglezakis, V. J., Moustakas, K. G. and Loizidou, M. D. (2007). Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column. *J. Hazard. Mater.*, 143(1-2); 575-581.
- Vieira, M. G. A., de Almeida Neto, A. F., Carlos da Silva, M. G., Nóbrega, C. C. and Melo Filho, A. A. (2012). Characterization and use of in natura and calcined rice husks for biosorption of heavy metals ions from aqueous effluents. *Braz. J. Chem. Eng.*, 29(3); 619–634.
- Wang, F., Pan, Y., Cai, P., Guo, T. and Xiao, H. (2017). Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. *Bioresour. Technol.*, 241; 482-490.
- Xie, Z., Guan, W., Ji, F., Song, Z. and Zhao, Y. (2014). Production of biologically activated carbon from orange peel and landfill leachate Subsequent treatment technology. *Journal of Chemistry*, article ID 491912, 9 pages.

- Yu, L. J., Shukla, S. S., Dorris, K. L., Shukla, A. and Margrave, J. L. (2003). Adsorption of chromium from aqueous solutions by maple sawdust. *J. Hazard. Mater.*, 100(1-3); 53-63.
- Yuvaraja, G., Subbaiah, M. V. and Krishnaiah, A. (2012). *Caesalpinia bonducella* leaf powder as bio-sorbent for Cu(II) removal from aqueous environment: kinetics and isotherms. *Indust. & Engg. Chem. Res.*, 51(34); 11218-11225.
- Zhang, F., Wang, B., He, S. and Man, R. (2014). Preparation of graphene-oxide/polyamidoamine dendrimers and their adsorption properties toward some heavy metal ions. *J. Chem. & Engg. Data*, 59(5); 1719-1726.

