POTENTIALS OF TURMERIC PLANT RHIZOMES FOR THE SORPTIVE REMOVAL OF DIVALENT METAL IONS

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Abstract: The performance of adsorbents, prepared from low cost tumeric for the removal of divalent metal ions was investigated. The adsorbents, coded as chemically modified biosorbent (MTB) and unmodified turmeric biosorbent (UTB) were characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). Protocols of batch experiment were followed for profiling several parametric factors. Equilibrium data were modeled using isotherm, kinetic, diffusion and thermodynamic equations. Results shows more developed pore size for the derived adsorbents which in turn presented higher sorption performance. In this study, sorption is best explained with the pseudo-second order model ($R^2>0.999$), following more than one form of transport mode. Sorption process is thermodynamically spontaneous. The positive $\Delta S°$ reflected an irregular increase of the randomness at the adsorbent/solution interface. The activation energy (A) values were higher than 42 $kJmol^{-1}$ indicating chemical reaction-based sorption processes (chemisorption) that also infer claims of the pseudo-second order model. The statistical test, comparing UTB and MTB indicates significant differences ($p<0.5$) for all the parametric factors. Overall, the study shows that MTB is a potential sorbent candidate for the uptake of divalent metal ions from wastewater, unveiling a removal efficiency of up to 95 % for divalent Cu, 94 % and 99 % Ni ions.

Keywords: Curcumin, equilibrium, isotherm, kinetic, sorption, metals, thermodynamic, turmeric

Introduction

Wastewater from numerous industries such as paints and pigments, glass production, mining operations, metal plating and battery manufacturing processes are known to contain contaminant such as heavy metal such as Pb, Cd, Cr, Ni, Zn, Cu and Fe (Bernard *et al.*, 2013). These metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems. Higher concentrations of divalent metals (Cu^{2+}, Pb^{2+} and Ni^{2+}) cause cancer of lungs, nose and bone relate. Acute poisoning of divalent metal ions cause headache, dizziness, sickness and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness (Malkoc and Nuhoglu, 2005).

Investigation into new and cheap methods of metal ions removal has been on the increase lately (Bernard *et al.*, 2013). Various methods including: filtration, chemical precipitation, adsorption, electro-deposition and membrane systems or even ion exchange process (Meena *et al.*, 2008).

In general, it has been documented that complexation with curcumin reduces the toxicity of the metals and some curcumin complexes with metals like Cu^{2+} and Mn^{2+} act as new metal-based antioxidants (Leung *et al*., 2013; Asti, 2009). The turmeric; Curcuma longa plant (Plate 1) is a perennial herb which belongs to the ginger family. The rhizome of turmeric plant is also referred to as the root and is the most useful part of the plant for culinary and medicinal purposes. Turmeric is valued for the yellow pigment curcumin (diferuloylmethane) which varies from 4 to 8% in the dried rhizomes (Chattopadhyay *et al.*, 2004). Curcumin in turn contains curcumin I (almost 94%), curcumin II (6%) and curcumin III (0.3%) (Fig. 1).

Curcumin forms strong complexes with most of the known metal ions. There are several papers published in the literature on complexes of curcumin with divalent metals like Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2}(Ferrari *et al.*, 2013; Khalil *et al.*, 2013). The structure and physical properties of these complexes depend on the nature of the metal ion, as well as the stoichiometry of the reaction conditions, which in turn decides their stability and reactivity. Curcumin is a monobasic bidentate ligand and forms stable complexes with almost all the metals (Fig. 2) and non-metals

Equilibrium and kinetics are key-factor for assessment of sorption parameters. Several empirical and theoretical models have been proposed for the studies of sorption phenomenon. Table 1 presents some of these mathematical relationships and models employed in this study with their physical quantities.


(a) (b)

Plate 1: (a) Turmeric plant (b) rhizome and rhizome powder

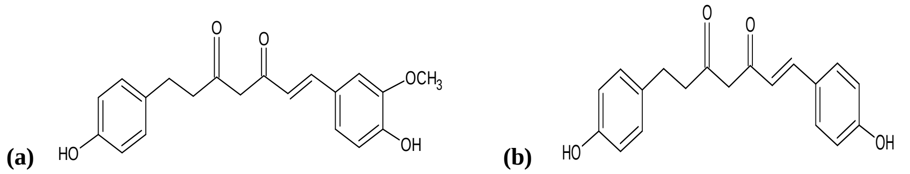

Fig. 1: Chemical Structures of (a) Demethoxycurcumin (curcumin II) and Bisdemethoxycurcumin (curcumin III)

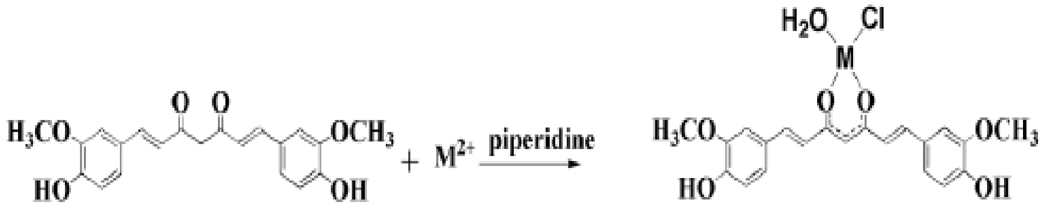

Fig. 2: Typical scheme for curcumin metal complexation (Annaraj *et al.*, 2004)

Table 1: Selected equilibrium and kinetics models for assessment of sorption parameters

Parameters	Models/Equations	Expression	References
Equilibrium	Mass balance	$q_e = \frac{V(C_o - C_e)}{M}$	(Itodo, 2018a;Mohamed, 2003).
	Sorption Efficiency	RE (%) = $\frac{C_o - C_e}{C_o} \times 100$	(Aderonke *et al* 2016)
Isotherm	Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_{mbc_e}}$	(Sha'Ato *et al*., 2018)
	Freundlich	$\log q_e = \log k_f + \frac{1}{n} \log C_e$	(Sha'Ato *et al*., 2018)
	Temkin	$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} lnC_e$	(Itodo *et al*., 2018b)
Kinetic	Pseudo first order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	(Araújo *et al*., 2004)
	Pseudo second order	$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e} t$	(Choi *et al* 1999)
Transport/Diffusion	Intra-particle diffusion	$q_t = k_{int} t^{1/2}$	(Itodo *et al*., 2018b)
	Film diffusion	$\ln(1 - F) = -k_{fd} t$ (F=qt/qe),	(Itodo *et al*., 2018b)
Thermodynamic	Van't Hoff	$\text{Log } k_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$	(Sha'Ato *et al*., 2018)
		$K_c = \frac{C_{Ae}}{C_e}$ $\Delta G = -RTlnK_c$ $A = \Delta H^\circ + RT$	(Abd EI-Latif *et al*., 2010).

q_e (mg/g)- amount of sorbate (mg) per unit mass (g) of sorbent; RE%-removal efficiency; q_e and q_t(mg/g) - amount of sorbate uptake at equilibrium and at time t respectively; k_1(min^{-1}) and k_2 constant ($g \cdot mg^{-1} \cdot min^{-1}$)- rate constants. k_{int} - intra-particle rate constant; F-fractional attainment of equilibrium (F=qt/qe), K_{fd} -liquid film diffusion constant; K_c is equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium, C_e is residual Concentration at equilibrium, R is gas constant (J/mole) and T is the temperature in Kelvin. ΔH and ΔS- Changes in enthalpy and entropy respectively, A- activation energy

For continuous search for cheap and available biomass with specific properties, this team considered a curcumin containing plant as bio-sorbent for the uptake of divalent metal ions. The aim of this study is the design of batch experiments to evaluate the sorption removal of aqueous phase metallic ions (Cu^{2+} and Ni^{2+}) using adsorbents derived from turmeric. This research work is limited to the preparation, characterization and utilization of turmeric in the treatment of simulated aqueous phase solution, contaminated with divalent metal ions.

Materials and Methods

All chemicals were of analytical grade except otherwise stated. Adsorbent characterization was based on classical and instrumental techniques. SEM (Phenomenon Prix, MVE016477830) and FT-IR (Agilent technologies 4000- 650) were used for surface morphology and functional group analysis. Heavy metal quantification was carried out using AAS () . Quality assurance was achieved by the use of untreated precursor as control and good laboratory practices. All standard and stock solutions were prepared following routine laboratory procedures.

Sampling and sample pretreatment

Fresh rhizomes of turmeric were harvested from different places in Mbarakom village and Akamkpa both in Cross River State, Nigeria. Turmeric samples and whole plant were taken to the botanical unit of Federal University of Agriculture Makurdi, for identification. Sample voucher number was documented along with other taxonomical facts. The methods reported by Olayinka *et al*. (2009) and Karthikeyan *et al*., (2007) were adopted for Size modification. The turmeric rhizomes were washed with water, soaked in warm water to extract colour, thoroughly and severally washed with water followed by rinsing with distilled water. Samples were dried, ground and sieved to pass through a < 2 mm aperture size sieve. The sieved samples were chemically treated with hydrogen peroxide at room temperature for about 24 h to oxidize the adhering organic matter, after which it was stored in a well label bottle as UTB for use.

The method documented by Wuana *et al*. (2016) was adopted for the chemical modification of the absorbent, MTB. In the preparation, 300 g of the washed UTB adsorbent was mixed with 500 mL of 1 mol dm^{-3} NH$_4$Cl. The mixture was heated at 120^{0}C for 30 min with constant stirring. The adsorbent was separated from water using funnel and washed with distilled water until the washing were free of color and the pH of wash solution was about 8. pH of the absorbent was determined using Hanna pH meter.

Characterization of adsorbent

Bulk density, dry density and porosity were investigated using method of Ekpete and Horsfall (2011) with slight modification. Attrition was by the method of Toles *et al.* (2000). Determination of iodine number was carried out using the protocol of Gimba and Musa (2007). Scanning electron microscopy (SEM) was used to study the surface morphology of the untreated and derived turmeric bio-sorbents. Fourier transform infrared (FTIR) spectroscopic analysis was used to study the surface chemistry of raw material of turmeric.

Batch equilibrium study: Batch experiments was designed to optimize parametric factors, assessing the effect of various operational parameters (initial solution pH, adsorbent dose, contact time, temperature and concentration) on characterization and adsorptive removal of divalent ions (Cu^{2+}, Pb^{2+} and Ni^{2+}). Adsorption kinetic experiment was performed by shaking 1g portion of the adsorbents in 50 mL aliquots of 100 mg/L metal solutions for 10, 30, 60, 120, 180 and 240 min on a mechanical shaker at room temperatures. The filterate was analyzed for equilibrium phase metal ions using AAS.

Results and Discussion

Physicochemical parameters of the adsorbent

Results of the physicochemical parameters of adsorbent coded as unmodified turmeric bio-sorbent (UTB) and Modified turmeric bio-sorbent (MTB) were reported as mean value and presented in Table 2.

Table 2: Physiochemical properties of adsorbent

S/N	Parameters	UTB	MTB
1	pH	6.50	6.44
2	Bulk density (g/cm^3)	0.031	0.033
3	Dry density (g/cm^3)	0.845	0.845
4	Attrition (%)	67.7	86.2
5	Iodine adsorption number (mg)	143	168

UTB-Unmodified Turmeric, MTB- Modified Turmeric Biosorbent

pH: This is an important factor in adsorbents production, depicting a good wash. The pH of UTB and MTB were found to be 6.5 and 6.4, respectively. It has been reported by Ahmedna *et al*. (2000) and Okieimen *et al*. (2004) that for most applications, carbon pH 6-8 is acceptable.

Bulk density: Bulk density, an essential characteristic of the carbon and is correlated to the starting material. Bulk density is one of the variables in the design of adsorption columns. A higher density carbon will generally not have to be generated as frequently as it will hold more adsorbate per unit volume. Results on bulk density of the unmodified turmeric (0.031g/m^3) and modified turmeric (0.033 g/m^3) indicates that both UTB and MTB has a low bulk density and makes it a good carbon for the design of adsorption column as it would not withhold more of the adsorbate per unit volume. The same trend agrees with a finding already documented for treatment of organic and inorganic pollutants in municipal wastewater by agricultural by-product based granular activated carbons (Wartelle and Marshall, 2001).

Attrition: Attrition is a measure of the mechanical strength of the adsorbent and it is an essential factor for understanding its relative loss during hauling, treatment, and regeneration. The % attrition of unmodified turmeric and modified turmeric are 67.72% and 86.23% respectively. The difference in the % attrition of the UTB and MTB is likely due to the chemical treatment involved in MTB method. This inference was documented by Toles *et a*l. (2000) and Bansode *et al*. (2003).

Iodine adsorption number: Iodine number is an essential factor used to characterize adsorbent performance. It is a measure of the micro pore level of the adsorbent and is obtained by the adsorption of iodine from solution by the adsorbent sample (Ekpete and Horsfall 2011). Sorbents with high iodine number performs better in removing small sized contaminants. High value indicates high degree of activation as documented by Aziza *et al*., (2008). It is often reported in mg/g and typical values range between 500-1200 mg/g (Raffiea *et al*., 2012). Lesser Iodine adsorption number value for the UTB (143.27) and MTB (167.51) is an indication that this adsorbent could be mesoporous and may find good application for medium size particles like dye of better performance as an adsorbent.

Surface morphology

SEM Characterization: The surface morphology of the turmeric biosorbent samples was studied by scanning electron microscopy. Plate 2 shows the micrographs of UTB and modified turmeric biosorbent (MTB).

From the results of the SEM micrographs, MTB is characterized by pore development. The presence of pores on the MTB creates high attraction for the adsorbate adsorption. It is also an indication required for high adsorption capacity of the metals as compared to UTB (Kadirvelu *et al*., 2005).

FT-IR Characterization: The active sites (functional groups) of unmodified and modified turmeric biosorbents (UTB and MTB) were investigated using FT-IR spectrometer (Agilent technologies 4000- 650). Spectra are presented in Figure 3. Table 3 illustrates the comparative FT-IR spectra characteristics of and MTB respectively. Results agrees as opined that plant cells are constructed by polysaccharide, protein, lipid composition, containing carboxyl, carbonyl, hydroxyl, amino and other functional groups which can bind with metal ions (Macfie and Welbourn 2000; Amir *et al*., 2004). The FTIR spectra of the adorbents displays numbers of similar adsorption peaks, indicating the complex nature of adsorbent. Interpretation in Table 3 and the similarities of the results is an indication of complete removal of residual chemical after pore size development.

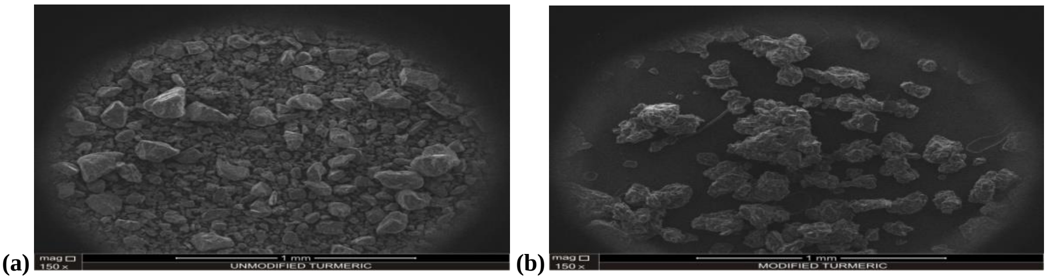

Plate 2: SEM Image of (a) UTB and (b) MTB

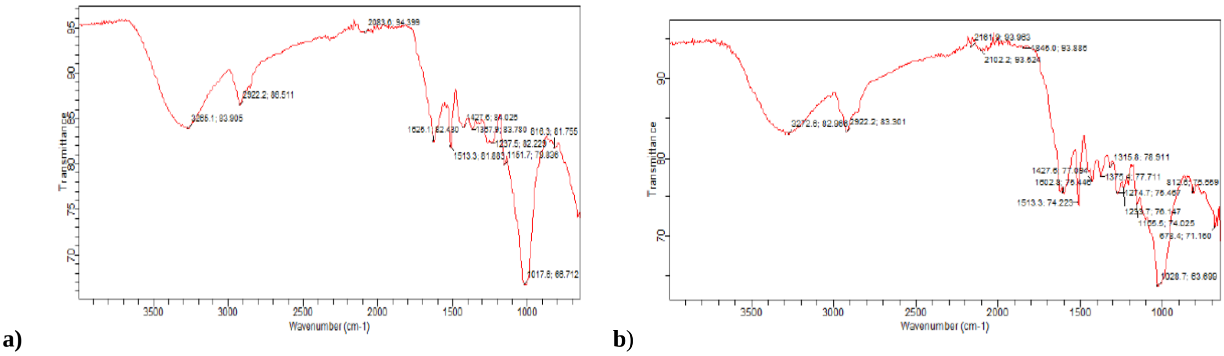

Fig. 3: FT-IR Spectrum of (a) UTB and (b) MTB

Table 3: FTIR spectral characteristics of adsorbents

Group frequency (cm^{-1})	Functional Group	Observed Frequency (cm^{-1})		Assignment
		UTB	MTB	
790-840	Alkenes	818.3	812.6	=C-H bend
1450-1600	Aromatic	1513	1513.3	Ring C=C bend
3500-3200	Alcohols, Phenols	3265.1	3272.6	O-H stretch, H-bonded
2850-3000	Alkanes	2922.2	2922.2	C-H stretch
1320-1000	Esters	1237.5	1315.8	C-O stretch
1020-1075	Ethers	-	1274.7	=C-O-C symmetric
		-	1028.7	& asym. stretch

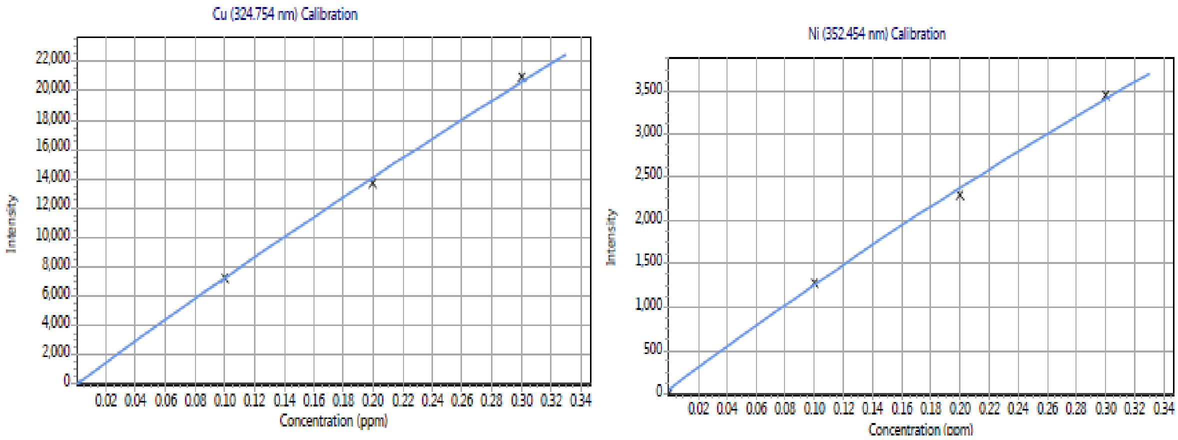

Fig. 4: Calibration curve Cu concentration

Batch adsorption studies

Figure 4 shows the level of linearity upon which the estimation of metal ions is relied. Their correlation coefficient values for Cu and Ni are 0.9995 and 0.9928 respectively. The curve passing through the origin and absolutely low intercept values depicts minimal or no deviation from the working principle, thus considering the $y = mx + c$ approximation in estimating equilibrium phase metal concentrations.

The role of the following parametric (Fig. 5) factors in the removal of divalent metals from aqueous solutions were investigated:

Effect of pH: this is one of the significant factors governing the adsorption of metal ions. The results show the effect of pH ranging from pH 3 to 11 on the adsorption of Cu and Ni ions on unmodified and modified turmeric (UTB and MTB). It was observed from Figure 16 to 18 that the removal efficiency of metal ions in the aqueous solution decreases at low pH values and increases with increasing pH of the solution. The removal of Cu-UTB was 40% and Cu-MTB was 59% at pH of 3 and it reached its maximum value of 66% for Cu-UTB and 61% for Cu-MTB at pH of 11. The influence of pH can be related with the fact that in an acid environment competition among metals and H$^+$ ions occurs and the metal retention in such condition is not essential. With increasing pH, electrostatic repulsion decreases owing to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption (Bhattacharya *et al*., 2006).

Effect of initial metal ion concentration: The observed behavior for effect of metal ion concentration can be attributed with the high driving power for the charge transfer. Result shows that metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific active sites, while at higher concentrations; lower adsorption yield is due to the saturation of adsorption sites. This agrees with the opinion of Bojic *et al*. (2004).

Effect of contact time: Equilibrium time is a crucial parameter for an optimal removal of metal ions in the waste water. It was observed that the adsorption of Cu and Ni ions by unmodified and modified turmeric was highly influenced by contact time.

Effect of temperature: Figure 5 shows that Cu-UTB and Ni-UTB increases with increase in temperature from 40 to 80 and decreases with increase in temperature for Cu-MTB and Ni-

MTB. These results indicated that the adsorption of Cu-UTB and Ni-UTB are exothermic in nature and Cu-MTB and Ni-MTB is endothermic in nature (Khattri and Singh, 2009).

Effect of adsorbent dosages: The maximum dose of adsorbent for Cu and Ni ions was found as 0.05 and 1.0, respectively. Figure 5 also indicates a decrease with increase in adsorbent dose for Cu-UTB, there is an Observed increase in percentage removal of metal ions with adsorbent dosage can be attributed to the availability of adsorption sites for metal adsorption (Garg *et al*., 2003).

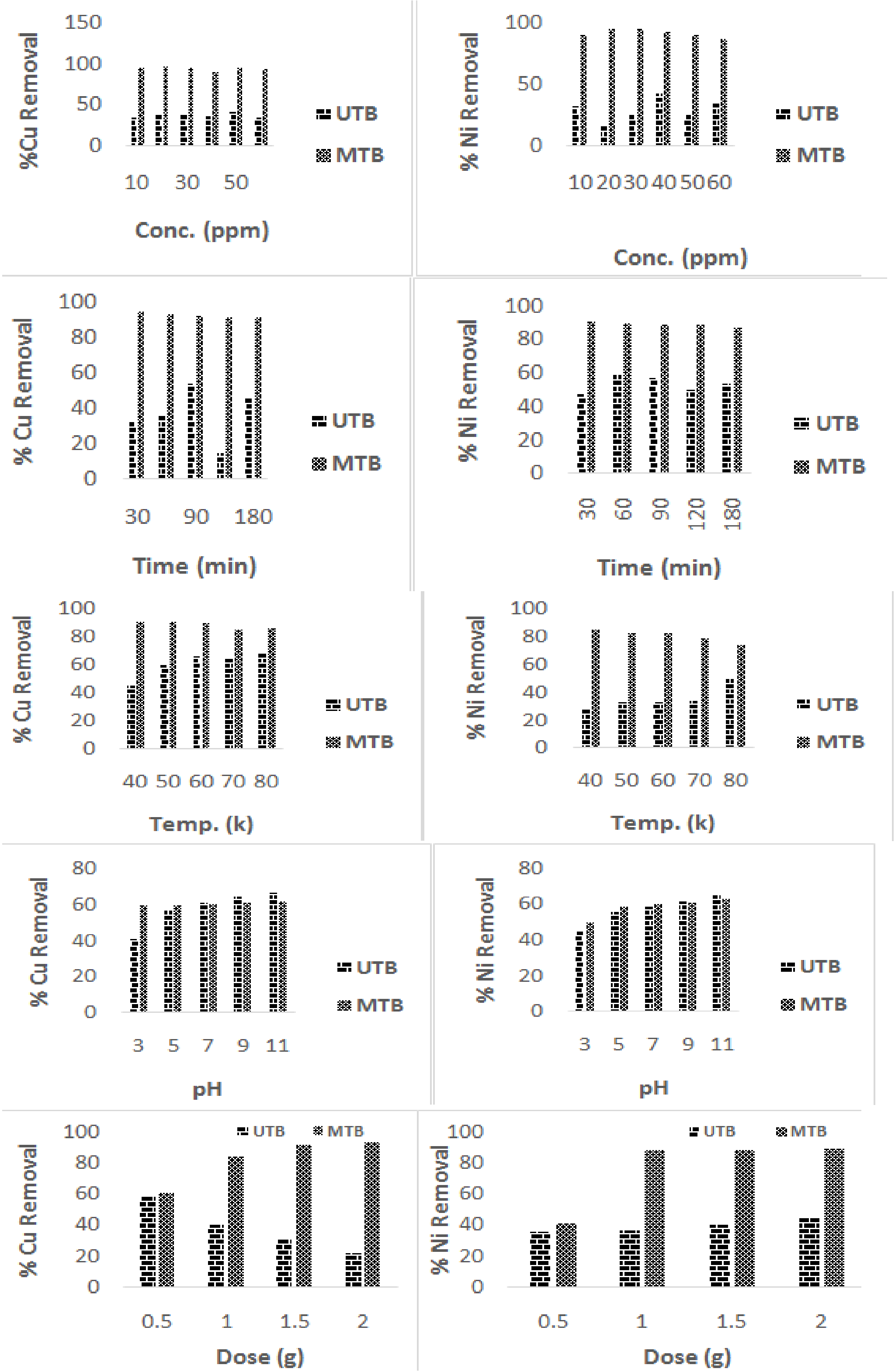

Fig. 5: Effect of parametric factors on removal efficiency of divalent metal ions

Table 4: Isotherm constants for cu and ni sorption on turmeric biosorbent

Isotherms	Constants	Values

		Copper (Cu)		**Nickel (Ni)**	
		UTB	**MTB**	**UTB**	**MTB**
Langmuir	R^2	0.989	0.948	0.599	0.970
	R_L	0.003	0.002	0.012	0.011
	q_m (mg/g)	21.008	0.527	37.037	0.206
Freundlich	R^2	0.975	0.904	0.674	0.993
	1/n	0.929	1.246	2.022	0.064
	K_f (L/mg)	17.988	1.954	3.732	23.768
Temkin	R^2	0.998	0.997	0.989	0.993
	b_T (KJ/mol)	2897.745	143.047	1345.045	184.069
	R_T (L/mg)	2477.572	2477.572	2477.572	2477.572

Isotherm studies

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at a constant temperature and its concentration in the equilibrium solution is called adsorption isotherm. Adsorption isotherm is important in the description of how solutes interact with sorbents. It describes some physical constants which explains certain sorption properties. Table 4 shows the isotherm parameters for adsorption of UTB and MTB biosorbents.

Langmuir isotherm: The equilibrium data for copper, nickel and lead has been correlated with the Langmuir isotherm (Figs. 6 and 7). In Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. A linear plot was obtained when 1/qe was plotted against 1/Ce over the entire concentration range. R^2 value of 0.989 for UTB, 0.948 for MTB onto copper, 0.599 for UTB, 0.970 for MTB onto nickel and 0.980 for UTB. They shows a good applicability of the model, indicating monolayer adsorption (Vinodhini and Das, 2010). The essential feature of the Langmuir isotherm was expressed by means of dimensionless constant separation factor (R_L). R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Result from this work shows adsorption is favorable for UTB and MTB for both Cu^{2+} and Ni^{2+}.

Freundlich isotherm: The Freundlich constants (K_F and n) were calculated from the slope and intercept of the linear plot (Figs. 8 and 9) of log q_e versus log C_e. The magnitude of the component 'n' gives an indication of the favorability of adsorption process and K_F is the constant related to the adsorption capacity. It has been shown that n>1, represents a favorable adsorption. The n value was found to be 1.246 for Cu-MTB and 2.022 for Ni-UTB which indicates favorable adsorption.1/n indicates the adsorption intensity of metal ions onto the adsorbent becoming more heterogeneous as its value gets closer to 0. A value of 1/n below 1 indicates a normal Freundlich isotherm while 1/n above 1 indicates co-operative adsorption. Hence, it is observed that our value; 0.929 for Cu-UTB, 0.0635 for Ni-MTB, 0.709 were not favorable with the model. The isotherm constants K_f and n were calculated from the linear form of the model and correlations coefficients of K_f and n are given in Table 4.

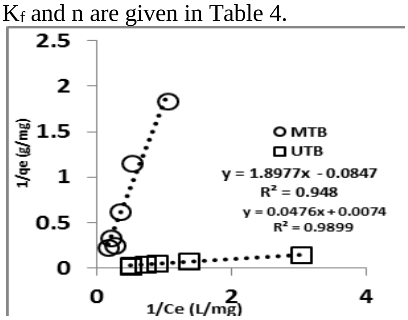

Fig. 6: Langmuir isotherm plot for Cu adsorption on turmeric biosorbent

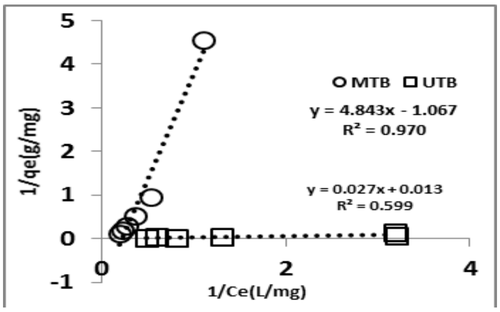

Fig. 7: Langmuir isotherm plot for Ni adsorption on turmeric biosorbent

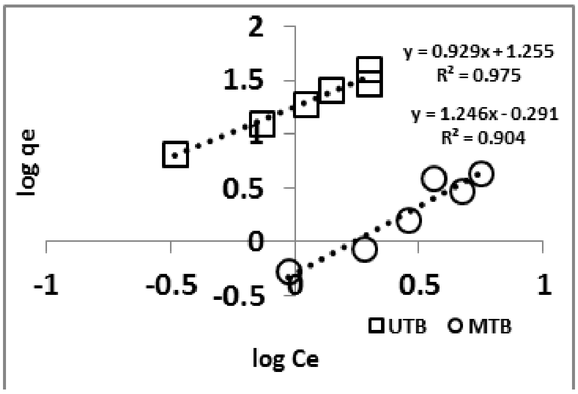

Fig. 8: Freundlich isotherm plot of Cu adsorption turmeric biosorbent

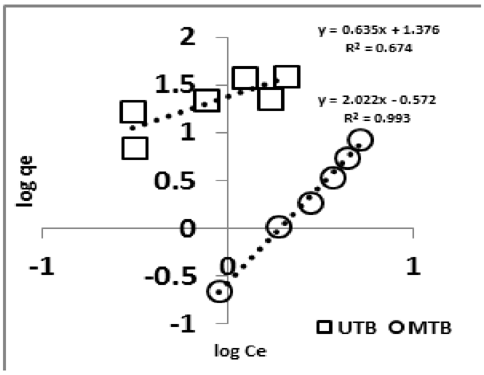

Fig. 9: Freundlich isotherm plot of Ni adsorption on turmeric biosorbent

Kinetic studies

Adsorption kinetics governs the rate of reaction, which determines the habitation time and is one of the important characteristics defining the effectiveness of an adsorbent. Kinetic constants help in drawing conclusions on the adsorption rate and mechanism (Arias, 2009). Table 5 shows the Kinetic studies of experimental constants for pseudo first-order kinetic and pseudo second-order kinetic. In order to test the suitability of the prepared adsorbents for the adsorption of metal ions, the data were analyzed using both pseudo first-order and second-order kinetics rate equations.

Pseudo first-order kinetics: A simple kinetic analysis of adsorption is the pseudo first order kinetic (Onal *et al*., 2007). It is required that q_e (calculated) and q_e (experimental) values falls within good precision. This was not so. R^2 values by the model are low (Cu-UTB 0.198, Cu-MTB 0.662, Ni-UTB 0.060). Therefore, the results suggest that the adsorption of metal ions by UTB and MTB is not in agreement with pseudo first-order.

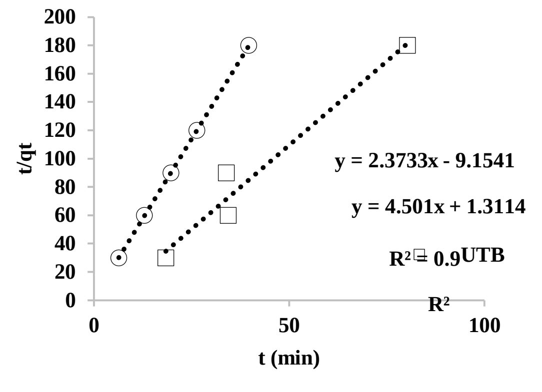

Fig. 10: Second Order Kinetic Plot of Cu Adsorption on Turmeric Biosorbent

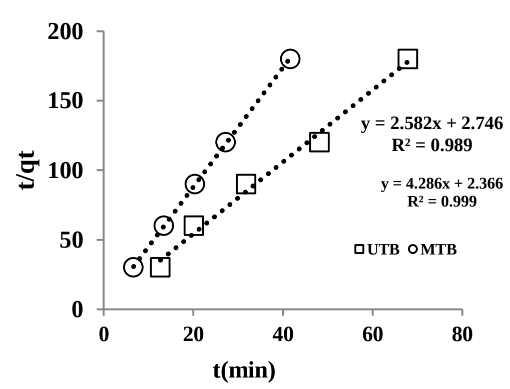

Fig. 11: Second Order Kinetic Plot of Ni Adsorption on Turmeric Biosorbent

Pseudo second-order kinetics: From Pseudo second-order kinetics plots (Figs. 10 and 11) values of R^2 obtained are 0.958 for Cu-UTB, 1 for Cu-MTB, 0.989 for Ni-UTB and 0.999 for Ni-MTB. The best fit for the experimental data was achieved by the application of second order kinetic equation. Ho and Mckay (2000) opined that the rate of adsorption sites is proportional to the square of the number of deserted sites. By this model, the rate restrictive step could be chemical adsorption. This result could be expected because the surface of adsorbent worked like chelate exchanger owing to the presence of curcumin in tumeric. Hence, sorption of metal ions by adsorbent (UTB and MTB) is well fitted in pseudo second-order kinetic model with $R^2>0.999$, compared to pseudo first-order kinetic model with $R^2<0.999$.

Table 5: Kinetic constant for Cu and Ni sorption on turmeric biosorbent

Model	Constant	Values			
		Copper(Cu)		Nickel (Ni)	
		UTB	MTB	UTB	MTB
First order	R^2	0.198	0.662	0.060	0.970
	K_1 (g/mg.min)	246.191	615.132	131.709	538.902
	q_e.exp(mg/g)	2.651	4.693	2.979	4.527
	q_e.cal (mg/g)	2.391	2.553	1.895	2.528
Second order	R^2	0.958	1.0	0.989	0.999
	K_2 (mg/g.min)	0.613	15.477	2.432	0.023
	q_e.exp(mg/g)	2.651	4.693	2.979	4.527
	q_e.cal (mg/g)	0.442	0.222	0.387	0.233

Table 6: Diffusion constants for Cu and Ni sorption on turmeric biosorbent

Diffusion Model	Constant	Values			
		Copper (Cu)		Nickel (Ni)	
		UTB	MTB	UTB	MTB
Intra-particle	R^2	0.402	0.877	0.011	0.979
	k_{id}(g/mg.min$^{1/2}$)	0.089	0.021	0.008	0.024
Film Diffusion	R^2	0.199	0.662	0.061	0.971
	K_{fd} (L^2/T)	-46.447	116.04	-24.837	101.66

Diffusion model

The intra-particle diffusion model was determined by the plot of the amount of sorbate adsorbed, q_t (mgg^{-1}) versus $t^{0.5}$ in Fig. 12. It can be observed that in this studies, a linear plot with the correlation coefficient values of $R^2<0.989$, 0.402 for Cu-UTB, 0.877 for Cu-MTB, 0.011 for Ni-UTB and 0979 for Ni-MTB were (Table 6). Higher value of k_{id} illustrate an enhancement rate of adsorption, whereas, larger k_{id} values illustrate better adsorption which is related to improved bonding between sorbate and sorbent particles (Erhan *et al*., 2004). The line in the plot for Cu-UTB, Ni-UTB and Pb-UTB does not pass through the origin, thus signifies that the intra-particle diffusion is not the only rate determining factor for this study (Biyan *et al.,* 2009).

The film diffusion model plots of ln (1-F) versus time was plotted for Cu-UTB, Cu-MTB, Ni-UTB Ni-MTB, Pb-UTB and Pb-MTB is presented in Fig. 13. The correlation coefficient values of (R^2) are predominantly low 0.199 for Cu-UTB, 0.662 for Cu-MTB and 0.061 for Ni-UTB. An exception to 0971 for Ni-MTB whose R^2 value was >0.970. This also implied that film diffusion model is not fit for determining the rate factor in the adsorption process. This model describes the movement of adsorbate across the external liquid film to the external surface sites on the adsorbent particle (Choy *et al.,* 2004). The k_{fd} values which were obtained from the intercept of the plot for all the adsorbent are higher than zero, but the lines do not pass through the origin, confirming that the liquid film diffusion model is not the rate determinant (Srivastava *et al*., 2006).

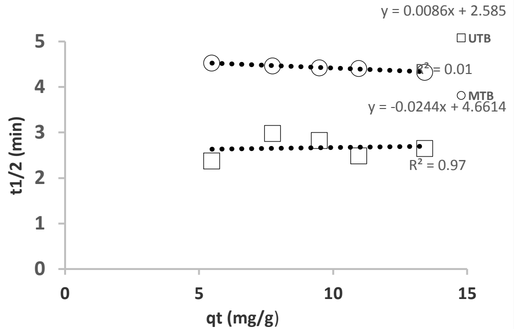

Fig. 12: Intra-particle Diffusion Model for Ni Asorption on Turmeric Biosorbent

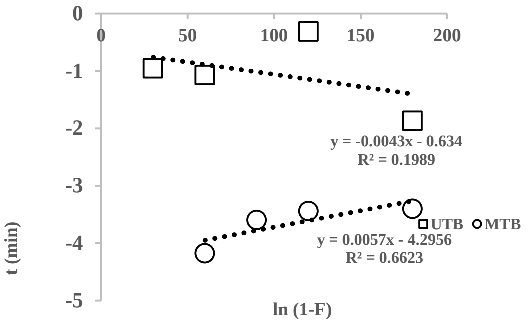

Fig. 13: Film Diffusion Model for Cu Adsorption on Turmeric Biosorbent

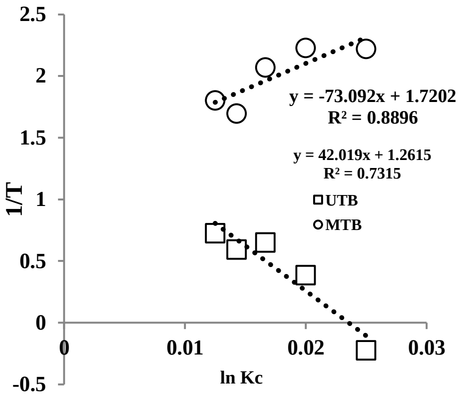

Fig. 14: Thermodynamics Plot for Cu Adosrption on Turmeric Biosorbent

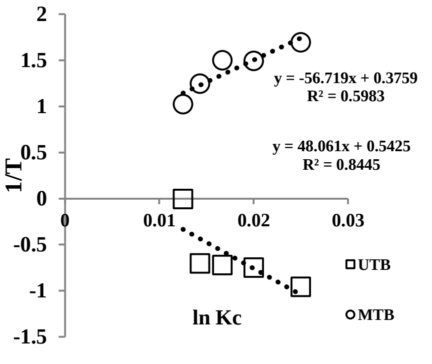

Figure 15: Thermodynamics Plot of Ni Adsorption on Turmeric Biosorbent

Adsorption thermodynamics

The thermodynamic paraters (ΔG˚, ΔH˚, ΔS˚ and A) related with the biosorption process were evaluated and presented in Table 7. The variation of temperature affects the biosorption of metal ions onto solid surfaces of biomass since the biosorption process is a reversible one. Increase in temperature is said to be in favoured of the endothermic side, while decrease in temperature is said to be in favoured of the exothermic side. The values of ΔGº, ΔSº, ΔHº, and A are calculated from the slope and intercept of the linear plot of ln k_c versus 1/T, respectively. The plots shown as Figs. 14 and 15 are linear over the entire range of temperature investigated. The negative values of ΔG˚ indicate spontaneity of each biosorption process. In general, the negative values of ΔGº for the adsorbents Cu-UTB (-11214.729 kJ/mol^{-1}); Cu-MTB (-6393.349 kJ/mol^{-1}) and Ni-UTB (-3230.712 kJ/mol^{-1}) indicates the exothermic nature of the adsorption (Vimonses *et al*., 2009). The increase in ΔG˚ with increase in temperature indicates less efficient biosorption at higher temperature. The positive values of ΔS° for Cu-UTB (32.937 kJ/mol^{-1}); Cu-MTB (24.154 kJ/mol^{-1}); Ni-UTB (7.197 kJ/mol^{-1}) and Ni-MTB (10.387 kJ/mol^{-1}) indicates that the degrees of freedom increased at the solid-liquid interface during the adsorption of metal ions onto adsorbents and reflected the affinity of adsorbent toward metal ions in aqueous solutions and could suggest some structural changes in adsorbents (Teker and Imamoglu, 1999). Furthermore, the magnitude of activation energy (A) gives an idea about the type of adsorption which is mainly diffusion controlled process or chemical reaction processes (Abd EI-Latif *et al*., 2010). Energies of activation, A, below 42 $kJmol^{-1}$ indicate diffusion-controlled processes, and higher values give chemical reaction-based processes.

Table 7: Thermodynamic parameters for metal ion sorption on turmeric biosorbent

Metal ion	Adsorbent	ΔS° (J mol^{-1}K^{-1})	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	A(kJ mol^{-1})
Cu	UTB	32.937	1399.5	-11214.729	1078.069
	MTB	24.154	804.543	-6393.349	3282.115
Ni	UTB	7.197	-1086.01	-3230.712	1391.566
	MTB	10.387	9202.231	-6106.905	11679.803

Statistical Tests of significance: Table 8 showed the level of significance ($p< 0.05$) between MTB and UTB for different parametric factors at 95% confidence intervals. The results showed that the p-value for the metal sorption was significant for the effects of concentration, time, temperature, pH and dosage. An exception to this is pH for Cu and Ni whose values were greater than 0.05. This is expected since both pH ranges were deliberately arrived at by thorough washing to achieve sludge free biosorbents.

Table 8: Comparing the level of significance of MTB and UTB ($p<0.05$)

Metals ions	Parametric Factor	P-Value	Comparison of MTB and UTB based on Removal efficiency
Cu	Concentration	0.010x10^{-10}	Significant
	Time	0.027x10^{-03}	Significant
	Temperature	0.0002	Significant
	pH	0.645	Not significant
	Dosage	0.006	Significant
Ni	Concentration	0.025x10^{-06}	Significant
	Time	0.031x10^{-05}	Significant
	Temperature	0.059x0^{-04}	Significant
	pH	0.721	Not significant
	Dosage	0.020	Significant
Pb	Concentration	0.004	Significant
	Time	0.030x10^{-03}	Significant
	Temperature	0.0006	Significant
	pH	0.025	Significant
	Dosage	0.0005	Significant

Conclusion

The potential use of turmeric as an adsorbent for copper and nickel was studied and established. Investigated isotherms shows slight deviation of applicability. Rate of the adsorption of the divalent metal ions is best explained with the pseudo-second-order kinetics model. Sorption is thermodynamically spontaneous with multi-mechanistic transport mode. Performance by chemically modified turmeric significantly differ ($p<0.05$) from the vice for virtually all the investigated parametric factors. Generally, the study indicates that the MTB is a good candidate as a low cost adsorbent for the adsorption of divalent metal ions from wastewater

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