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Utilization of Agro-waste Material as Potential Adsorbent for Removal of Cu(II) and Ni(II) Ions From Aqueous Phase

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ABSTRACT

The chemically treated agro-waste as adsorbent for the purification of wastewater contaminated with heavy metals. Pumpkin husk as an excellent adsorbent for removal of Cu(II) and Ni(II) ions. It depended on the controlling parameters such as pH, contact time, initial metal ion concentration, adsorbent dosage, and temperature. pH 5 was found to be suitable for Cu(II) and Ni(II) ions. Equilibrium, thermodynamic, and kinetic data were well fitted (R^2=0.997). Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° have also been evaluated, and it has been found that the adsorption process was spontaneous, endothermic, and randomness in nature. The Langmuir adsorption isotherm data fitted well. The kinetic experimental data correlated well with the second order kinetic model. The results concluded that the treated pumpkin husk (TPH) was an eco-friendly, economically cheap and effective adsorbent in the removal of Cu(II) and Ni(II) ions from aqueous solution.

Key words: *Adsorption, Agro-waste, Isotherm, Kinetic, Metal ion, Thermodynamic.*

1. INTRODUCTION

Heavy metal pollution is an environmental problem of worldwide concern [1]. Toxic heavy metals such as copper, chromium, zinc, iron, lead, mercury, cadmium and nickel contaminants in aqueous streams, arising from the discharge of untreated metal contain effluents into water bodies, even at low concentration, these metal ions can be toxic to living beings [2,3]. Some methods have been developed to remove heavy metals from waste water before discharge into the water bodies. These methods include membrane filtration, chemical coagulation, oxidation, solvent extraction, reduction, precipitation, ion exchange, reverse osmosis, dialysis, and adsorption by coated carbon [4-8]. The most of these methods are expensive so are not affordable. They also have limited application as they cannot remove metals as low concentration [9]. This has, therefore, led to the use of agricultural wastes in removal of heavy metals. Agricultural wastes are characterized by ready availability, affordability, eco-friendly, and high uptake capacity for heavy metals due to the presence of functional groups which can bind metals to effect the removal of heavy metal from effluents. The aim of the study was to the removal Cu(II) and Ni(II) ions from aqueous solution using treated pumpkin husk (TPH) as a bioadsorbent. The research involved the modification of pumpkin husk with HCl and NaOH and investigation of some experimental conditions such as pH, contact time, initial concentration, adsorbent dosage, and temperature as it relates to adsorption of the metal to the adsorbents. It also involved the use of Freundlich and Langmuir adsorption isotherm models to fit in the data. A kinetic study using pseudo first order and pseudo second order were also used to investigate the mechanism of adsorption.

2. MATERIALS AND METHODS

2.1. Materials

The stock solution was prepared by dissolving 3.929 g of copper sulfate and 2.6364 g of nickel sulfate in 1 L of double distilled water. Different concentrations of metal solution were prepared by dissolving required amount of stock solution. All reagents used were of analytical grade without purification.

2.2. Preparation of Adsorbent

The adsorbent pumpkin husk was collected from a kitchen and local market. The collected bioadsorbent was extensively washed under water to remove any particulate. This biosorbent was cut into small pieces and immersed in 0.1M of hydrochloric acid for 24 h. It is then filtered, washed with deionized water, and the pH is kept neutral. After acid treatment, alkali treatment is done by immersing the filtrate in

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0.1 M sodium hydroxide solution for 24 h. It is further filtered and drained with deionized water, and the pH is brought to neutral. The sample is then sun dried, ground separately using mortar and pestle and stored in a dried vessel. They are separated according to the different particle sizes using British Standard Sieves (BSS). The adsorbent was called as TPH.

2.3. Batch Adsorption Studies

The metal solutions used in this study were prepared as the stock solutions of known concentration was taken in the 250 ml conical flask, BSS 30 and 1 g of adsorbent was added separately and maintained the pH 5 for Cu(II) and Ni(II) ions then solution was stirred in mechanical shaker with 120 rpm at room temperature. For a wide range, contact time is 0-60 min. After that, the solution was filtered; absorbance and concentration of the solution were determined by Atomic Absorption Spectrophotometer (PerkinElmer, Model AA400). The amount adsorbed of the TPH for Cu(II) and Ni(II) ions was calculated from the mass balance equation given in equation:

$$q=(C_0-C_e)\times V/m$$

The percentage removal of metal ion was calculated from equation:

$$\%\ \text{adsorbed}=[(C_0-C_e)/C_0]\times 100$$

Where, "q" is the amount adsorbed (mg/g), C_0 and C_e are the initial and equilibrium concentration (mg/L) of metal ions in solution, "V" is the volume of metal solution (L), and "m" is the weight of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of TPH

The scanning electron microscope (SEM) analysis was performed to observe the surface morphology of the adsorbents before and after metal ion adsorption. The SEM images for TPH before and after metal interaction are shown in Figure 1. SEM analysis revealed that there were significant changes on the surface of adsorbents after interaction with metal ions. Before metal ion adsorption, TPH displayed a smooth and dense surface texture. After interaction with Ni(II) ion, the surface of TPH become irregular and flakes-like surface was observed and foam-like net anchored on the surface of the TPH corresponding to the adsorbed Cu(II) ion on the surface.

The moisture content of TPH was found to be 1.49%. The lower the percentage moisture, the better the yield, and quality of adsorbent. The ash content from this study was found to 7.9% for TPH. This is favorable because the ash serves as interference during the adsorption process. The lower the ash content, the better the material. This is favorable because the ash serves as interference during the adsorption process.

3.2. Effect of pH

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate [10]. pH variation is one of the most important parameters controlling the uptake of toxic metals from wastewater and aqueous solutions [11]. Effect of pH on adsorption was conducted at ranges of 1-9 in each solution. The percentage adsorption increases with pH, and it attains maximum at pH 5 for Cu(II) ion Ni(II) ion, and thereafter, it decreases with further increase in pH. This scenario will cause competition between H_3O^+ and metal ions for active sites on the surface of adsorbents [12-14]. As the solution pH increased the concentration of H_3O^+ ion in the solution decreased, lowering the competition of metal ion for active sites. The optimum pH for adsorption of Cu(II) and Ni(II) was recorded at pH 5 in Figure 2. The decrease in removal of metal ions at higher pH may be due to solvation and hydrolysis of metal ion to form soluble

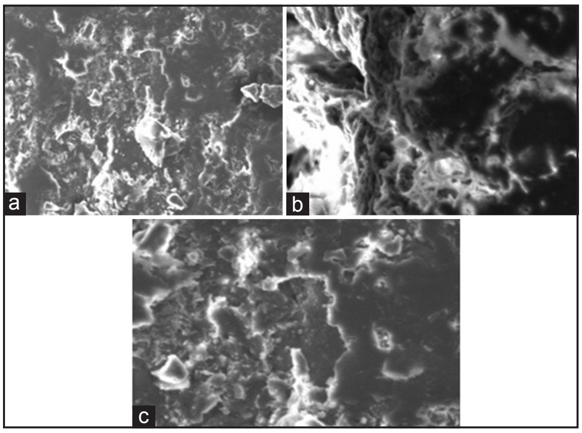

Figure 1: Scanning electron microscope images of (a) treated pumpkin husk (TPH), (b) Ni(II) ion loaded TPH, and (c) Cu(II) ion loaded TPH.

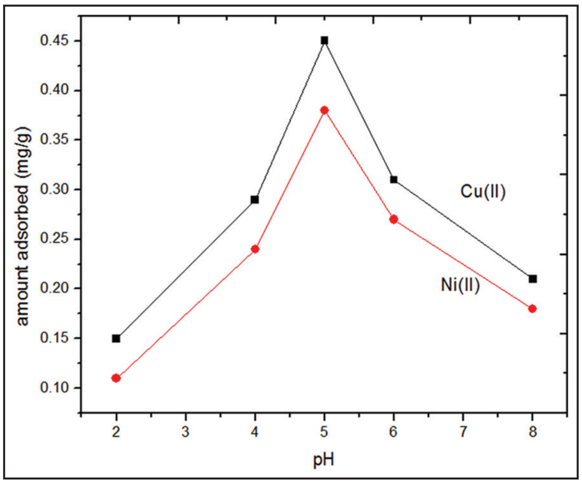

Figure 2: Effect of pH on adsorption of Cu(II) and Ni(II) ion by treated pumpkin husk.

hydroxylated complexes that compete for active sites. Moreover, the nature of ionization on the surface of adsorbents at specific pH may also cause the reduction of metal ion removal [15].

3.3. Effect of Contact Time

Contact time is an important factor in batch sorption process [16]. Experiments for contact time were conducted with Cu(II) and Ni(II) ion concentrations of 10 mg/L with a dose of 1 g of TPH at pH 5, size: 0.38-0.46 mm, and room temperature for 1 h. Figure 3 shows the effect of contact time on adsorption of Cu(II) ion and Ni(II) ion by TPH. Maximum removal efficiency for Cu(II) was 88.72% and Ni(II) ion was 81%, respectively. Therefore, removal efficiency of Cu(II) ion was higher than Ni(II) ion. The rate of bivalent ion removal was very rapid during the first 20 minutes and after that it attains equilibrium. Initially, there were a large number of vacant active binding sites in TPH, and consequently, large amount of Cu(II) and Ni(II)ions were bound rapidly onto TPH. The binding site was shortly become limited and the remaining vacant surface sites are difficult to be occupied by ions due to the formation of repulsive forces between the ions on the solid surface and the liquid phase [17,18]. Besides, the mesopores become saturated at the initial stage of adsorption where the metal ions are adsorbed. As a result, the driving force of mass transfer between liquid and solid phase in an aqueous adsorption system decreases with time elapse. Further, the metal ions have to pass through the deeper surface of the pores for binding and encounter much larger resistance which slowing down the adsorption [19]. Adsorption rate of Cu(II)and Ni(II) ion on TPH was found to be relatively much faster than those reported for some other bioadsorbates [11].

3.4. Effect of Initial Concentration

The initial metal ion concentration is an important factor to be considered in adsorption studies. The rate of adsorption of an adsorbent for a metal ion is dependent on the initial concentration of metal ion present in solution. The effect of initial Cu(II) and Ni(II) ion concentration on adsorption by TPH is presented in Figures 4 and 5; it is seen that the amount adsorbed capacity of the TPH for this two metal ions increased with increase in the initial concentration of metal ions. This increase is simply due to the presence of more metal ions in solution available for sorption. This increase in concentration increased the driving force overcoming resistances to mass transfer between the adsorbent and adsorbate species which led to the increase in adsorption observed [20].

3.5. Effect of Adsorbent Dosage

The effect of adsorbent dosage level on adsorption of Cu(II) ion and Ni(II) ion is shown in Figures 6 and 7. The amount adsorbed for bivalent ions was found to increase with an increase in the mass of adsorbent.

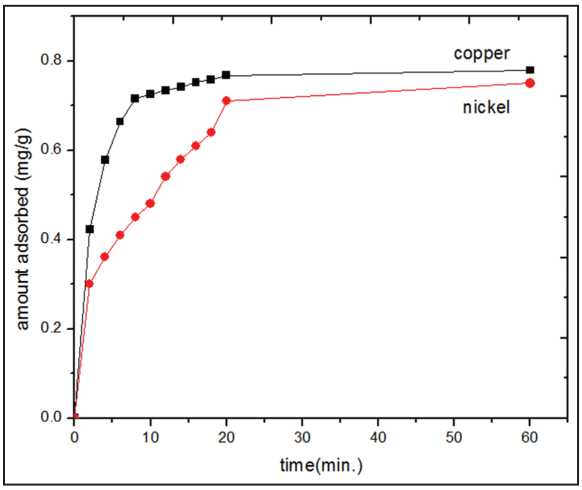

Figure 3: Effect of contact time on adsorption of Cu(II) and Ni(II) ion by treated pumpkin husk.

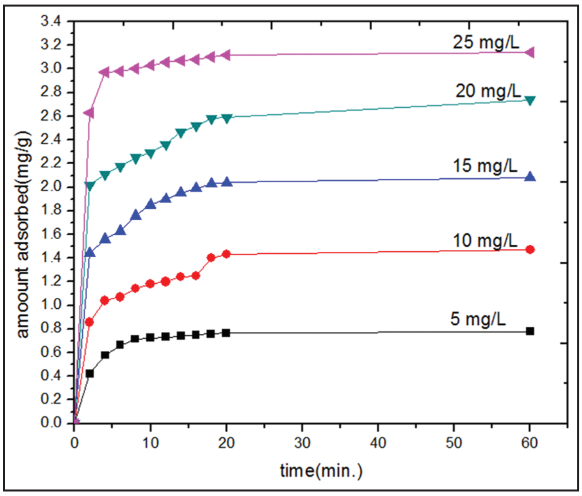

Figure 4: Effect of initial concentration on adsorption of Cu(II) ion by treated pumpkin husk.

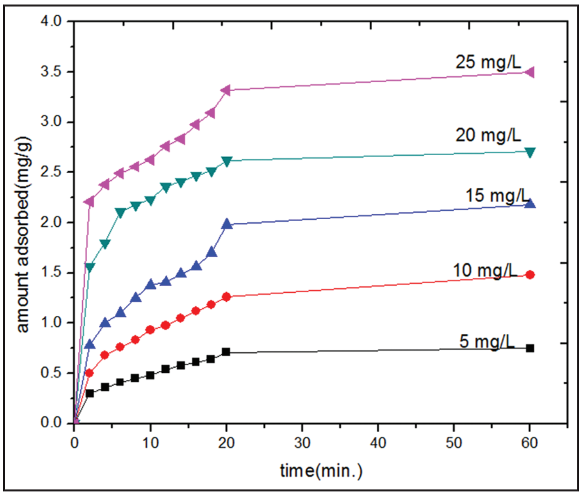

Figure 5: Effect of initial concentration on adsorption of Ni(II) ion by treated pumpkin husk.

This is because of the availability of more and more binding sites for complexation of bivalent ions [20].

The amount adsorbed for Cu(II) and Ni(II) ions using TPH was 0.779 mg/g and 0.74 mg/g, respectively. The partial aggregation among the available active binding sites may act for less removal of bivalent ions at high dosage [21]. Furthermore, due to lack of active binding site, the lower removals were obtained at low adsorbent doses [22].

3.6. Effect of Temperature

Adsorption as the effect of temperature was carried out in different temperatures such as 294 K, 301 K, and 308 K, and remaining parameters were kept constant and found that adsorption increases with increase in temperature (Figures 8 and 9). Adsorption equilibrium is a thermo-dependent process; it may be attributed increased temperature which increases the kinetic energy of the metal ions and thus weakening the forces of attraction between the metal ions and the adsorbent [23]. Temperature plays a major role in the adsorption of heavy metals on the surface of adsorbent and has two major effects on the adsorption process, increase in the temperature increases the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles as the liquid viscosity decreases with increase in temperature and other affects the equilibrium capacity of the adsorbate [18,24].

3.7. Thermodynamic Parameters

To determine the thermodynamic parameters on the adsorption, the temperature variation experiments were conducted at 294 K, 301 K, and 308 K with an initial metal ion concentration. Based on the fundamental thermodynamic concept, it is assumed that in an isolated system energy cannot be gained or lost, and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered to determine which process will occur spontaneously [25,26]. The equilibrium constant K_c of the adsorption is defined

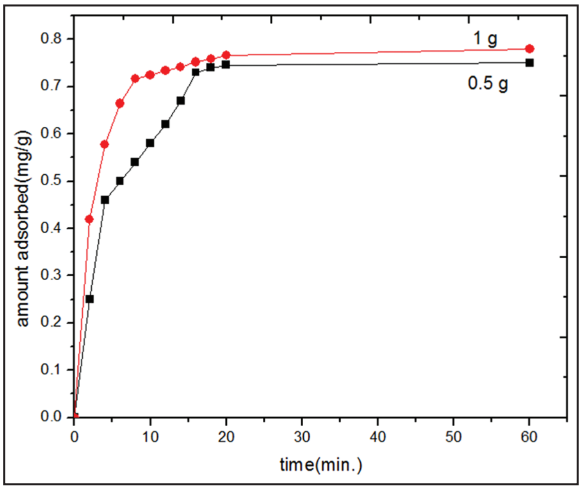

Figure 6: Effect of dosage on adsorption of Cu(II) ion by treated pumpkin husk.

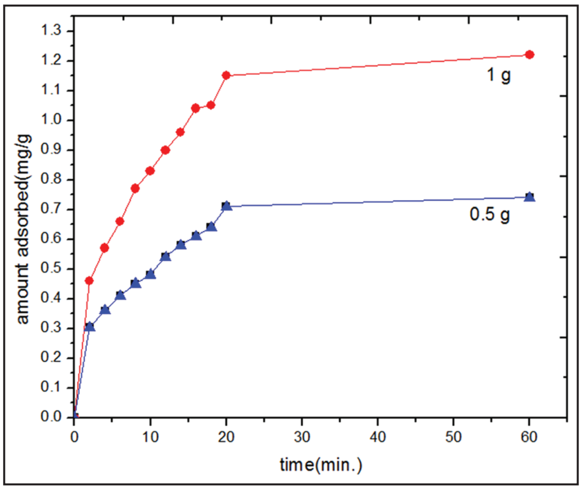

Figure 7: Effect of dosage on adsorption of Ni(II) ion by treated pumpkin husk.

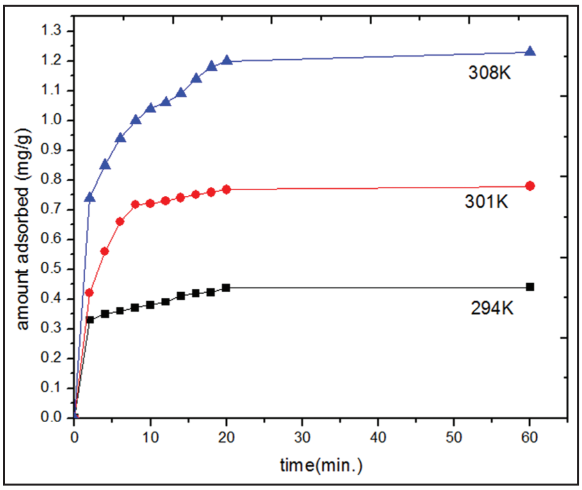

Figure 8: Effect of temperature on adsorption of Cu(II) ion by treated pumpkin husk.

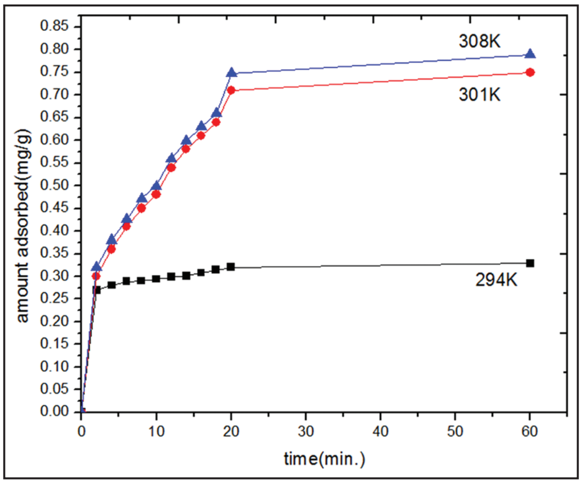

Figure 9: Effect of temperature on adsorption of Ni(II) ion by treated pumpkin husk.

as $K_c=C_i/C_e$, where C_i and C_e are the concentration of metal ion on the TPH and residual metal ion concentration at equilibrium, respectively. In this case, the activity should be used instead of concentration to obtain the standard thermodynamic equilibrium constant of the adsorption system [27].

The free energy change of the sorption reaction is given by the following equation [22].

$\Delta G°=-RT \ln K_c$

Where, R is gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K).

The Gibbs free energy change, ΔG°, can be represented as follows:

$\Delta G°=\Delta H°-T\Delta S°$

As a plot of ΔG° versus T was linear. Enthalpy change, ΔH°, and entropy change, ΔS°, were determined from the slope and intercept of the plots (not given). The free energy of the process at all temperatures was negative and changed with the rise in temperature. The negative values of ΔG° at all temperatures studied are due to the fact that adsorption is spontaneous. The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption of metal ions onto TPH [27]. Positive values of ΔH° indicate the endothermic nature of the adsorption process. Table 1 summarizes the values of these thermodynamic parameters. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.

3.8. Adsorption Isotherm

Adsorption isotherm describes the equilibrium relationships between adsorbent and adsorbate. The Langmuir [28] and Freundlich [29] adsorption isotherms were used to fit the equilibrium data. Its applicability was judged with the correlation coefficient (R^2). Langmuir equation can be linearized by the following form:

$C_e/q_e=1/Q_o b+C_e/Q_o$

Where, C_e is the equilibrium concentration in liquid phase (mg/L), Q_o is the monolayer adsorption capacity (mg/L), and b is the Langmuir constant related to the free adsorption energy (L/mg).

Freundlich equation can be linearized by the following form:

$\log q_e=\log K_F+1/n \log C_e$

Where, K_F is a constant indicative of the adsorption capacity of the adsorbent (mg/g), and the constant 1/n indicates the intensity of the adsorption. The linear plot of Langmuir isotherm for metal ions adsorption onto TPH and the calculated parameters along with regression coefficient (0.978 and 0.928) are in Figures 10 and 11 and Table 2, respectively. The maximum adsorption capacity for complete monolayer coverage was found to be 5.41 and 7.63 mg/g,

Table 1: Thermodynamic parameters for the adsorption of Cu(II) and Ni(II) ions onto TPH.

Metal ion	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Cu(II)	294	−2446.7	25.50	0.318
	301	−3775.0		
	308	−3783.2		
Ni(II)	294	−2241.8	23.32	0.309
	301	−3431.7		
	308	−3548.3		

TPH: Treated pumpkin husk

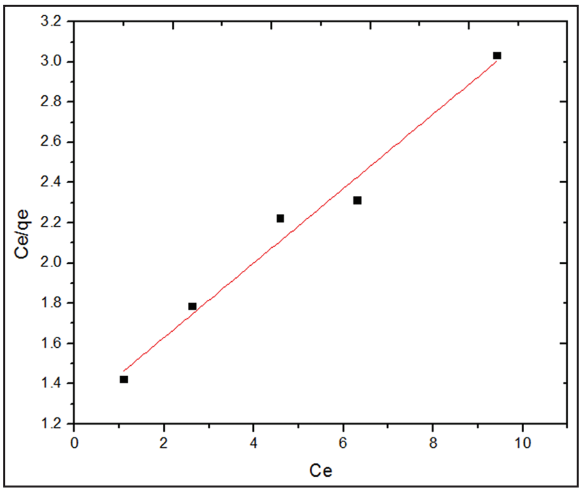

Figure 10: Langmuir adsorption isotherm for Cu(II) ion by treated pumpkin husk.

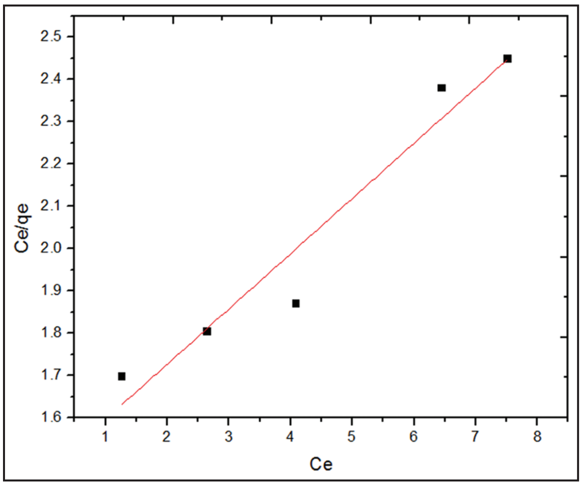

Figure 11: Langmuir adsorption isotherm for Ni(II) ion by treated pumpkin husk.

respectively, and regression coefficient values clearly suggest that Langmuir isotherm follows a good relation of Cu(II) and Ni(II) onto TPH. The "b" is the adsorption constant related to the affinity of binding sites (L/g), and lower values of "b" (0.147 for Cu(II) and 0.089 for Ni(II)) indicate that the particles radius of TPH were small toward adsorption [28]. Separation factor R_L an essential characteristic of Langmuir isotherm model was calculated by the following equation: $R_L=1/(1+bC_o)$.

The R_L values (Cu(II) are 0.558 and Ni(II) is 0.596) revealed that this adsorption onto TPH is favorable as the values lie between 0 and 1 [28].

The linear plot of Freundlich equation for Cu(II) and Ni(II) ions adsorption and the calculated parameters are shown in Figures 12 and 13 and Table 2, respectively. The Freundlich isotherm model the R^2 values are (0.907 for Cu(II) and 0.866 for Ni(II)), respectively. K_F is a Freundlich constant that shows adsorption capacity on heterogeneous sites with non-uniform distribution of energy level and "n" shows the intensity between adsorbate and adsorbent. The calculated values of "n" (Table 2) prove that the adsorption of Cu(II) and Ni(II) ions onto TCMH is favorable as the magnitude lies between 1 to 10.

3.9. Adsorption Kinetics

Kinetic studies are significant for any adsorption processes. Adsorption kinetics not only describes the adsorption mechanism of metals on adsorbents but also describe the metal adsorption rate which controls the contact time of metals at the solid-liquid interface [29]. The adsorption mechanism depends on the physical and chemical characteristics of adsorbent and adsorbate, pH of medium, temperature, contact time, and mass transport process. First order kinetic studies were conducted at pH 5 with five initial Cu(II) and Ni(II) concentrations.

The linear form of pseudo first order kinetic model [30] is as follows:

$$\log(q_e\text{-}q) = \log q_e - k_{ad}\, t/2.303$$

The adsorption rate (k_{ad}) is calculated from linear regression analysis from the slope of the linear plot of experimental data $\log(q_e\text{-}q)$ versus t. The linear plot of the experimental data and the calculated parameters are shown in Figures 14 and 15 and Table 3, respectively. The experimental data are not well fitted for pseudo first order kinetic equation as the R^2 were low. The kinetic data were also analyzed by pseudo second order equation [31] and the linear form as:

$$t/q_t=1/k^2\, q_e^{\,2}+t/q_e$$

Where, k_2 is the constant of pseudo second order rate, q_e is the adsorption capacity at equilibrium, and q_t is the adsorption capacity at time "t." The equilibrium adsorption capacity and the order rate constant were calculated from the slope and the intercept of the plot t/q_t against "t." The graphical interpretation of the data for second order kinetic model and calculated parameters are shown in Figures 16 and 17 and Table 3, respectively. A good fitted R^2=0.997 linear plots are obtained from experimental data while the calculated values of q_e also agreed with the experimental values. This finding revealed that the

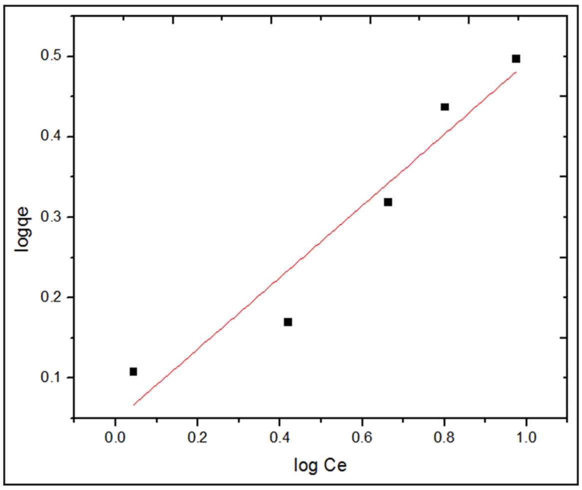

Figure 12: Freundlich adsorption isotherm for Cu(II) ion by treated pumpkin husk.

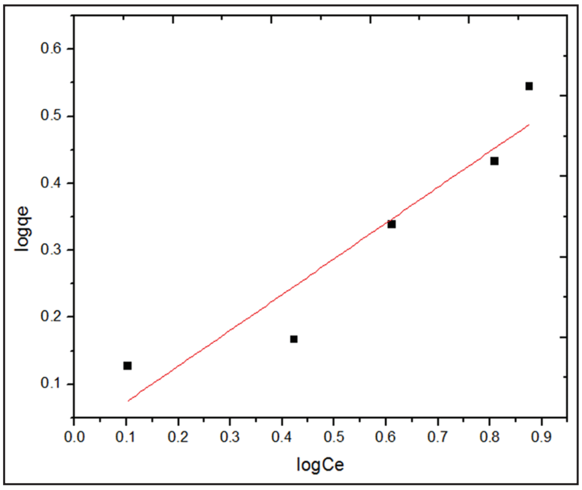

Figure 13: Freundlich adsorption isotherm for Ni(II) ion by treated pumpkin husk.

Table 2: Langmuir and Freundlich model parameters for the adsorption of Cu(II) and Ni(II) ions TPH.

Metal ion	Langmuir isotherm			Freundlich isotherm	
	Q_O	B	R_L	K_F	N
Cu(II) ion TPH	5.41	0.147	0.558	1.12	2.25
Ni(II) ion TPH	7.63	0.089	0.593	1.05	1.88

TPH: Treated pumpkin husk

copper and nickel adsorption onto TPH follows the pseudo second order mechanism, and the chemical adsorption process controls the adsorption rate. It was found that equilibrium adsorption capacity increased with an increase in initial metal ion concentration. The adsorption capacity increased from 0.78 to 3.14 mg/g for copper and 0.75-3.49 mg/g for nickel, respectively.

Table 3: Kinetic parameters for Cu(II) and Ni(II) ions adsorption onto TPH.

Metal ion	First order	Second order
Cu(II)	k_{ad}=0.1865	q_e=2.18
	R^2=0.948	k_2=0.285
		R^2=0.997
Ni(II)	k_{ad}=0.121	q_e=2.09
	R^2=0.886	k_2=0.103
		R^2=0.98

TPH: Treated pumpkin husk

When C_o was increased from 5 to 25 mg/L. The calculated values of equilibrium adsorption capacities were well agreed with the experimental values for the pseudo second order kinetic model.

3.10. Desorption

The possibility or regeneration of the adsorbent and recovery of the metal ions can be explored using desorption study. Desorption was carried out using batch experimental method. In this study, the adsorbent was regenerated using 0.1N NaOH. After the treatment, the metal loaded adsorbent with NaOH, the extent of desorption was found 42%.

4. CONCLUSION

The adsorption of copper and nickel from aqueous solution using TPH as the low-cost eco-friendly adsorbent was investigated in batch process. The adsorbent was characterized by SEM. The optimum pH value was found to be 5. The Langmuir adsorption isotherm was best fitted to the experimental data

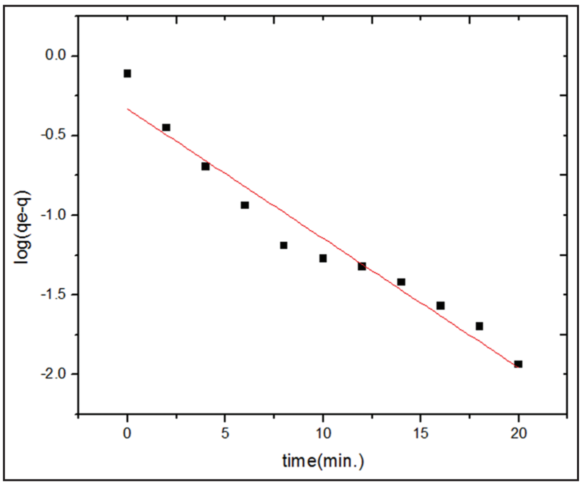

Figure 14: Linear plot of pseudo first order equations for Cu(II) ions onto treated pumpkin husk.

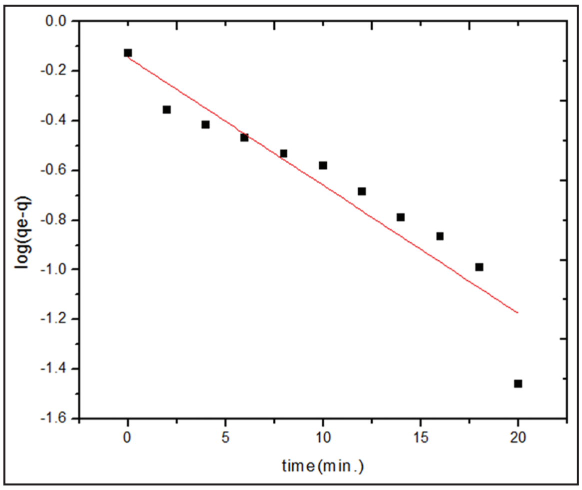

Figure 16: Linear plot of pseudo second order equations for Cu(II) ions onto treated pumpkin husk.

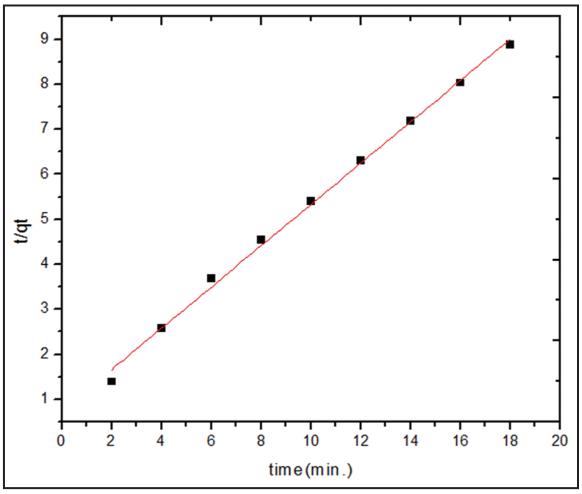

Figure 15: Linear plot of pseudo first order equations for Ni(II) ions onto treated pumpkin husk.

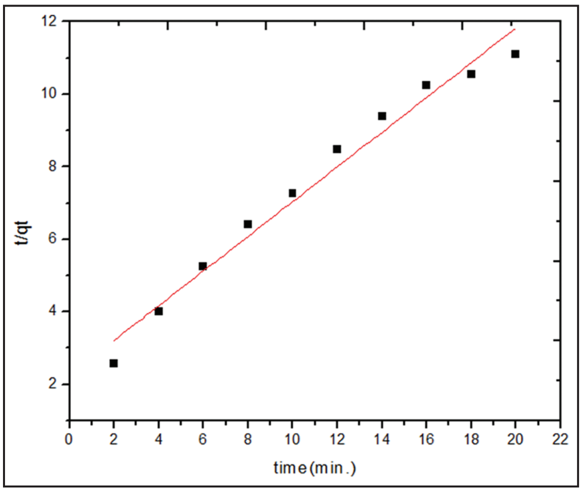

Figure 17: Linear plot of pseudo second order equations for Ni(II) ions onto treated pumpkin husk.

with a maximum adsorption capacity. Adsorption kinetics of copper and nickel adsorption onto TPH followed the pseudo second order kinetic model. Thermodynamic analysis suggests that the removal Cu(II) and Ni(II) ions from aqueous solution by TPH were a spontaneous, endothermic, and randomness. After adsorption, the adsorbent was successfully regenerated using 0.1 N NaOH. Therefore, the present findings suggest that a new source of adsorbent TPH used as an inexpensive and eco-friendly and effective adsorbent for the removal of Cu(II) and Ni(II) ions from wastewater and industrial effluent.

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