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Competitive biosorption of Ni (II) and Cu (II) ions from aqueous solutions onto chemically prepared carbon from *Acacia nilotica*

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ABSTRACT

The application of chemically activated (Phosphoric) Acacia nilotica leaves (PAN) for the removal of heavy metals Cu (II) and Ni (II) metal ions from aqueous solution was studied in a batch mode system. Adsorption of Ni (II) is more effective than adsorption of Cu (II) from aqueous solution by using PAN. PAN was characterized by using FTIR, SEM and XRD. Equilibrium, sorption, isotherms and kinetics are investigated. The effect of initial pH, contact time, initial metal concentration and adsorption dosage of Cu (II) and Ni (II) onto PAN have been investigated. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Adsorption isothermal data could be well interpreted by the Langmuir model. The rate of adsorption was found to be confirmed by pseudo-second-order kinetics with a good correlation of R^2 *value [Ni (II) 0.988 and Cr (II) 0.971]. Desorption studies of metals using PAN also was conducted. These results suggest that Acacia nilotica leaves have a low-cost adsorbent potential for the heavy metal removal from waste water.*

Keywords: Adsorption, *Acacia nilotica* leafs, isotherm, SEM, Desorption

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INTRODUCTION

Environmental pollution by heavy metals has become one of the most hazard problems due to their dangerous effect on aquatic flora and fauna even in relatively low concentrations. Several heavy metal ions such as copper, nickel, cadmium and lead have been included in the U.S. Environmental Protection Agency's list of priority pollutants [1]. Copper leads to toxic effects including liver damage and gastrointestinal disturbances. Nickel is a well-known human carcinogen, particularly in human lung cancer [2]. Among these metals Nickel is known to be essential to humans, animals, and plants but they can also have adverse effects if their availability in water exceeds certain threshold values. Therefore such removal of heavy metal from waste stream before discharge to public water is of primary concern.

Activated carbons, with their high porosity, are extensively used in industrial purification and chemical recovery operations. This is due to their extended specific surface area between 500 and 2000 m^2/g, their high pore volume and the presence of surface functional groups, especially oxygen groups [3]. The adsorption capacities of activated carbons strongly depend on their porosity, surface area, pore volume, pore size distribution. Activated carbon is a carbonaceous material processing a higher porosity due to which it is commonly used in variety of applications, concerned principally with the removal of chemical species by adsorption from the liquid or gas phase [4]. Since agricultural and food wastes are generated in large scale and are rather inexpensive, these materials are considered potential precursors for the preparation of low-cost adsorbents and have been thoroughly studied as such, with several recent reviews on the subject [5],[6]. Numerous agro-waste biomaterials have been used for the production of activated carbons, such as moss peat [7], coconut husk [8], coirpith [4], rice husk [9], tea leaf [10] and almond husk [11], have been reported for the removal of toxic metals from aqueous solutions. Activated carbon can be made from many substances containing high carbon content. The raw material has a very large influence on the characteristics and the performance of activated carbon.

Activated carbons could be produced by either physical (thermal) activation or chemical activation. In physical activation, steam or CO_2 is used for mild oxidation of the precursor which includes two processes, carbonization under an inert or reducing atmosphere followed by an activation step. In chemical activation, a dehydration agent, such as H_2SO_4, $ZnCl_2$, H_3PO_4 or alkaline metal compounds is used. In the thermal treatments for carbonization and activation, an external heating source such as a tubular furnace is normally adopted. H_3PO_4 is widely used for the process as it can be removed easily after activation of carbons by washing with hot and cold water. However phosphoric acid is preferred because it does not encounter with corrosion problem, in efficient chemical recovery and other environmental disadvantages associated with $ZnCl_2$ and other activants [12].There has been very little or perhaps nil study using H_3PO_4 as a chemical activating agent for carbon derived from rice husk and can be obtained cheaply from the agro industries.

In the external heating, the thermal process may take several hours, even up to several days to reach the desired level of activation so that the process incurs extra processing costs. Another problem lies in the furnace that is the thermal gradient from the hot surface of the particle to its interior. This situation affects the quality of the prepared activated carbons [13]. As a novel method for preparation of activated carbon, recently a great attention has been paid to the microwave heating. The main advantage of the microwave heating is the reduction of the treatment time which reduces the energy consumption as well. The main difference between MW devices and conventional heating systems is the manner of heating. Microwaves supply energy directly to the carbon bed. Energy transfer is not by conduction or convection as in conventional heating, but microwave energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction. Therefore, finding ways to use this agricultural by-product profitably will benefit date farmers substantially and offers an interesting alternative for their disposal.

The aim of the paper is to prepare an eco friendly microwave treated *Acacia nilotica* leaves as an agricultural waste for the depollution of water effluents and to find out the suitability and applicability of carbon prepared by different treatments (microwave and chemical) of *Acacia nilotica* to uptake metal ion from simulated waste water. Many physical and chemical treatment methods including adsorption, coagulation, precipitation filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of water containing effluents [14].

The removal of metals from aqueous solution by using chemically and microwave activated *Acacia nilotica* leaves has been investigated for various parameters such as initial pH, using this *Acacia nilotica* carbon reveal that the recovery of the metal from adsorbent is possible. *Acacia nilotica* having a high surface area, so it's very easy for the adsorption studies [16]. From this reference *Acacia nilotica* leaf is selected for the adsorption of heavy metals. To find out the suitability and applicability of carbon prepared by different treatments of *Acacia nilotica* to metal ion Ni (II), Cu (II) from simulated waste water. Due to its operational simplicity and relatively low-cost adsorption is growing in popularity and application.

EXPERIMENTAL SECTION

Preparation of phosphoric acid assisted *Acacia nilotica* (PAN)

The leaves of *Acacia nilotica* used in this work were collected locally from Coimbatore district, Tamilnadu. It was air-dried and powdered in a grinder. Dried *Acacia nilotica* treated with conc. H_3PO_4 for to vary concentrations in the range of 30% - 60% by volume. The slurry was kept at room temperature for various time spans in the range of 16 - 28 h to ensure the access of the H_3PO_4 to the *Acacia nilotica*. After mixing, the slurry was placed in a MW heating apparatus (MW71E, SAMSUNG). After a heating power of 100 W - 600 W and microwave radiation time of 10 min - 4 min, the carbonized sample were washed with 0.5 M NaOH, hot water and cold distilled water until the pH of the washing solution reached 6 - 7, filtered and finally dried at 150°C in hot air oven for 6 h. The PAN was then stored in an air-tight container for later experimental use.

Preparation of Adsorbate

Copper sulfate pentahydrate ($CuSO_4.5H_2O$) and nickel sulfate hexahydrate ($NiSO_4.6H_2O$), (Spectrum Reagents and Chemicals). All other chemicals used in this study were analytical grade. A stock solution (1000 mg/L) of Cu (II) was prepared by dissolving accurately weighed $CuSO_4.5H_2O$ and $NiSO_4.6H_2O$) in 1000 mL double-distilled water. Working copper solutions were prepared just before use by appropriate dilutions of the stock solution. A stock solution of 1000 mg/l of Ni (II) was prepared by dissolving ultra pure nickel sulphate [$NiSO_4 \cdot 6H_2O$] in double distilled water, acidified with nitric acid to prevent hydrolysis. Working copper solutions and nickel solutions were prepared just before use by appropriate dilutions of the stock solution. Adsorption experiments were conducted to investigate the influence of adsorption parameters such as pH, adsorbent concentration, activating temperature, contact time and initial concentration on Ni (II) and Cu (II) uptake by using PAN as adsorbent.

Optimization of PAN Preparation Conditions

In order to optimize the preparation conditions of the PAN, Taguchi experimental design method was used [17]. An L16 orthogonal array with four operational parameters each in four levels was used to evaluate the corresponding optimal values. These variables and their values are summarized in **Table 1.** The complete design matrix of the experiments and the obtained results are shown in **Table 2**. Iodine is considered as probe molecules for assessing the adsorption capacity of adsorbents for solutes of molecular sizes less than 10 Å. Iodine number was normally listed as specification parameter for PAN. Therefore, the responses were iodine number (Y_2, mg/g), yield (Y_1, %) was obtained at 25°C ± 1°C on the basis of the standard Test method. The yield of the carbon samples was estimated according to,

$$Y = \frac{M}{M_0} \times 100 \tag{1}$$

where M is the weight of PAN and M^0 is the weight of air dried *Acacia nilotica* leaves.

Table 1 Designs and levels

Independent variables	Symbol	Range and levels			
		1	2	3	4
Radiation power (W)	A	100	200	300	400
Radiation time (min)	B	10	8	6	4
Concentration of H_3PO_4 (%)	C	30	40	50	60
Impregnation time (h)	D	16	20	24	28

Table 2 Experimental design matrix and result

Runs	VARIABLES			
	A	B	C	D
1	1	1	1	1
2	2	1	1	1
3	3	1	1	1
4	4	1	1	1
5	1	1	1	1
6	1	2	1	1
7	1	3	1	1
8	1	4	1	1
9	1	1	1	1
10	1	1	2	1
11	1	1	3	1
12	1	1	4	1
13	1	1	1	1
14	1	1	1	2
15	1	1	1	3
16	1	1	1	4

Characterization of the adsorbent

The surface morphology of PAN was identified by using SEM technique (Jeol jsm-6390). A Fourier transforms infrared spectroscopy (SHIMADZU, IR Affinity-1) with KBr pellet was used to study surface functional groups of the PAN, with a scanning range of 4000 - 400 cm^{-1}. The zero surface charge (pH_{ZPC}) of PAN was determined by using the solid addition method. The ability of PAN in the adsorption of Ni (II) and Cu (II) in aqueous solution is finding out by batch isotherm and kinetic studies. The concentration of Ni (II) and Cu (II) in single was determined using a double beam UV-vis spectrophotometer (SHIMADZU UV-2450) of the wavelength of 232 nm and 245 nm. Surface characterization of PAN was done by SEM and XRD.

Batch mode studies

A stock solution of $NiSO_4$ $.6H_2O$ (1000mg/L) and $CuSO_4.5H_2O$ were prepared and suitably diluted accordingly to the various initial concentrations. Adsorption studies were carried out at room temperature (27 ± 5^oC). Batch adsorption studies were carried out using 0.2g of adsorbent for each bottle, the adsorption experiments were carried out with 50 mL of solution of required concentration and pH of the solutions varied from 2 to 10 in a bench shaker at a fixed shaking speed of 120 rpm. The resulting mixture was filtered (Whatsman filter paper No.41) and the initial and final concentrations of the metal ions were determined by UV-2450 vis spectrophotometer. The pH of the solution was adjusted using 0.1M HCl and 0.1M NaOH. The experiments were carried out for various adsorbent dosages, different initial Ni (II) ions concentration, for various contact time and different initial pH of the solution. The stock solution of $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$ were prepared for the concentration of 1000 ppm and it was diluted to various required concentrations. From the initial and final concentration, percentage removal can be calculated by

$$\%\ of\ removal = \frac{C_0 - C_F}{C_0} \times 100 \quad (2)$$

where C_o - initial concentration of nickel in mg/L, C_F- final concentration of nickel in mg/L. The data obtained in batch mode kinetics were used to calculate the equilibrium metal uptake capacity. It was also calculated for adsorptive quantity of nickel by using the following expression.

$$q_e = \frac{v(C_O - C_F)}{W} \quad (3)$$

where qe is the equilibrium metal ion uptake capacity in mg/g, v is the sample volume in litre, Co the initial metal ion concentration in mg/L, Ce the equilibrium metal ion concentration in mg/L and w is the dry weight of adsorbent in grams.

Effect of Adsorbent Dose

To observe the effect of adsorbent dose on metal adsorption, different amounts of adsorbent varying from 0.2 g/ 50 ml, 0.4 g/50 ml, 0.6 g/50 ml, 0.8 g/50 mL and 1 g/50 ml were added into initial concentration of 100 mg/L Cu (II) and Ni (II) in single solution. The mixtures were shaken in 250 mL stoppered flasks at room temperature at suitable pH until the equilibrium time was reached.

Effect of Solution pH

To study the effect of solution pH on metal adsorption, 100 mg/L initial concentration at different pH values (2 - 9) was agitated with 0.2 g of PAN in a mechanical orbital shaker at room temperature. The effect of pH on Ni adsorption was studied by varying the pH from 2.0 to 9.0. The concentration of Ni (II) and Cu (II) solution used for this study was 100 mg/L and the adsorbent dose was 0.2 g. The initial pH was written as pH_i and the solution pH after adsorption was also measured and written as pH_f. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl solutions.

Effect of Initial Metal Concentration and contact time

In order to study the effect of initial metal concentration on the adsorption uptake, nickel solutions with initial concentrations of 50 - 200 mg/L with varying the adsorbent dose of 0.2 g/50mL of PAN. In this case, the solution pH was kept as constant. The contact time necessary to reach equilibrium depends on the initial metal concentration. It has been shown that the adsorption capacity increases with this concentration, and the rate of adsorption on the surface should be proportional to a driving force times an area.

Adsorption isotherm

Adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when adsorption process reaches on equilibrium state. Equilibrium studies were undertaken to understand the behavior of the adsorbent at an equilibrium condition. Equilibrium data are basic requirements for the design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the metal ion on to the adsorbent. The results obtained on the adsorption of nickel were analyzed by the well-known models given by Langmuir, Freundlich, and Temkin isotherms. For the sorption isotherms, initial metal ion concentration was varied while the pH of the solution and adsorbent weight in each sample held constant. The sorption isotherms were realized with PAN at different solutions at different pH.

Langmuir isotherm

Langmuir model is the simplest theoretical model related to monolayer adsorption on the surface with finite number of available identical sites [18].The linear form of Langmuir equation is derived as: (4)

$$\frac{C_e}{q_e} = \frac{1}{Q_e K_L} + \frac{1}{Q_e} C_e \qquad (4)$$

where Q_e (mg/g) and K_L (dm^3/g) are Langmuir constants related to adsorption capacity and rate of adsorption.

Freundlich isotherm

Freundlich isotherm expression is an empirical equation assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [19]. The well-known logarithmic form of the Freundlich isotherm is given by:

$$\log q_e = \log k_f + {}^{1}\!/_{n} \log C_e \qquad (5)$$

where K_f (mg/g), (l/mg) and 1/n are the Freundlich adsorption constant and a measure of adsorption intensity.

Temkin isotherm

Temkin assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy [20]. The Temkin isotherm has been used in the form of:

$$q_e = B \ln A + B \ln C_e \qquad (6)$$

where B=RT/b, b and A, R and T are the Temkin constant related to heat of sorption (J/mol), equilibrium binding constant (l/g), gas constant (8.314 J/mol K) and absolute temperature (K).

Adsorption Kinetics

The kinetics describes the rate of adsorbate uptake on activated carbon. In order to identify the potential rate controlling steps involved in the process of adsorption, four kinetic models were studied and used to fit the experimental data from the adsorption of Ni (II) and Cu (II) onto PAN. These models are the pseudo-first-order, pseudo-second-order, Elovich and intra-particle kinetic models.

Desorption

Desorption helps to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal. After adsorption experiments the metal loaded carbon was separated out by filtration using Whatsman filter paper No. 42 and the filtrate was discarded. The metal loaded carbon was given a gentle wash with double-distilled water to remove the non-adsorbed metal if present. The metal loaded samples were agitated with distilled water by adjusting the initial pH from 2 to 7. The desorbed metals in the solution was separated by centrifugation and analyzed as before.

RESULTS AND DISCUSSION

Characterization of PAN

Zero surface charges

The influence on the solution pH on the metal uptake can be explained on the basis of the pH zero point charge or isoelectric point of the adsorbent. The value of the pH necessary to affect a net zero charge on a solid surface in the absence of specific sorption is called the point of zero charge, pH_{ZPC}.

The zero surface charge of PAN was determined by using the solid addition method [21]. The experiment was conducted in a series of 250 mL glass stopper flasks. Each flask was filled with 50 mL of different initial pH $NaNO_3$

solutions and 0.2 g of PAN. The pH values of the $NaN0_3$ solutions were adjusted between 2 to 9 by adding either 0.1 M HNO_3 or 0.1 M NaOH. The suspensions were then sealed and shaken for 2 h at 150 rpm. The final pH values of the supernatant liquid were noted. The difference between the initial pH (pH^0) and final pH (pH^f) values ($pH = pH^0 – pH^f$) was plotted against the values of pH0. The point of intersection of the resulting curve with abscissa, gave the pH_{zpc}. The point of zero charge of PAN is found to 5.05.This results indicated that the pH_{zpc} of PAN depended on raw materials and activated agency.Fig.1. shows the zero point charge of PAN. The zero point charge (pH_{ZPC} =5.05 for PAN) is below the solution pH (pH =7) and the negative charge density on the surface of PAN increased, which favours the adsorbtion of Ni (II) and Cu (II) [22].

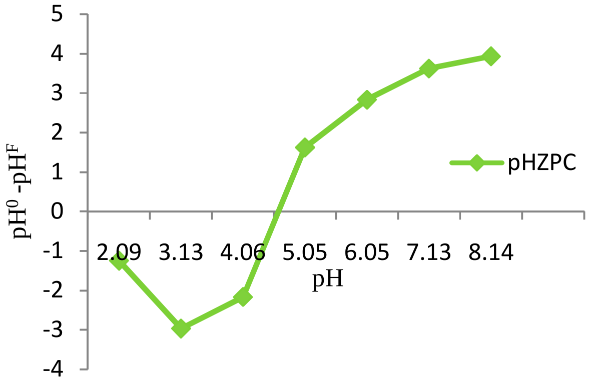


Fig. 1. Zero point charge of PAN

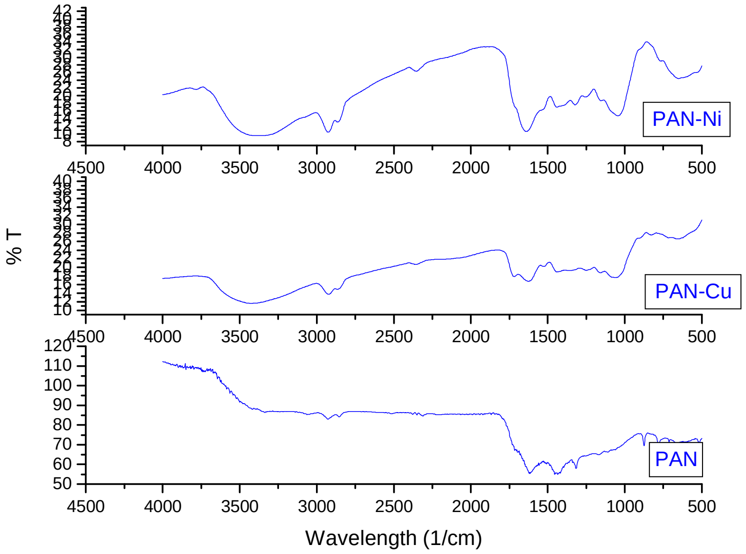


Fig. 2. FTIR results of PAN before and after Ni (II), Cu (II) adsorption

Functional group analysis of PAN

Functional groups in PAN before and after were determined by use of Fourier-transform infrared spectroscopy, at room temperature, by use of a Shimadzu, IR Affinity-1 spectrometer. KBr pellets were prepared from the samples, and the scanning range was 4000–400 cm^{-1}. Surface functional groups were detected by Fourier-transform infrared spectroscopy.Figs.1a. ,1b and 1b 1c shows the FTIR spectra of PAN before and after adsorption of Ni (II) and Cu (II) ions from aqueous solution respectively. The FTIR studies of the PAN have confirmed the presence of hydroxyl groups and carboxylic groups. The peak around at 3414cm^{-1} can be assigned to the –OH stretching vibration mode of hydroxyl functional groups. The broad band between 1325 and 1109 cm^{-1} has been assigned to C–O stretching in alcohols and phenols. The Biosorption of Cu (II) and Ni (II) onto PAN may likely be due to electrostatic attraction between these groups and the cationic metal molecules. After the adsorption of Cr (VI) on all activated carbons, there was a small shift in wave number and some of the wave number regions were not observed. This observation indicated the participation of adsorption of Cu (II) and Ni (II) on PAN activated carbon.

Characterization of PAN

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM) at different magnification; the results are shown in Fig.3. It was evident that the surface morphology of the activated carbon was different before and after adsorption. It can be seen from the micrographs that the external surface of PAN before is full of cavities (Fig.3) compared with PAN after (Fig.4 and Fig 5) and quite irregular as a result of activation and the pores were different sizes and different shapes. It is clear that the adsorbents have considerable number of heterogeneous pores, a cave- like, uneven and rough surface morphology, where there is a good possibility for metal to be trapped and adsorbed. Fig.6. shows the XRD results of PAN after the adsorption of Cu (II) and Ni (II) adsorption. Adsorption may lead to changes in the molecular and crystalline structure of the adsorbent and, hence, the molecular and crystalline structures of the adsorbent and changes thereof, provide valuable information about the adsorption reaction. From XRD analysis of PAN, we concluded that activation was complete in the preparation of PAN as activated carbon because of it diffraction profiles of broad peaks; the absence of sharp peaks was indicative of a predominantly amorphous structure, the broad peaks seem to occur at approximately 2h = 20º, 26º, and 44º, similar to the peaks of crystalline carbonaceous structures such as graphite.

Fig. 3. SEM structure of PAN before

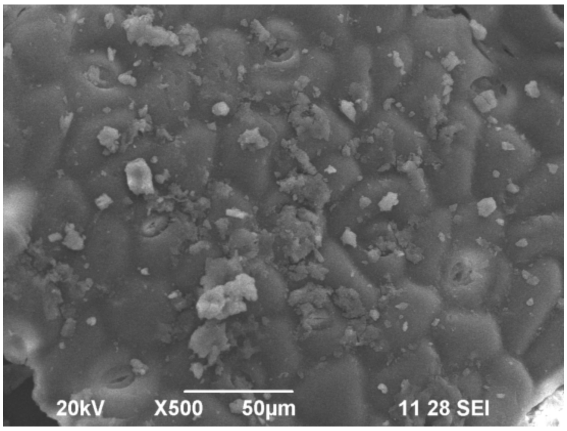


Fig. 4. SEM structure of PAN -Ni (II)

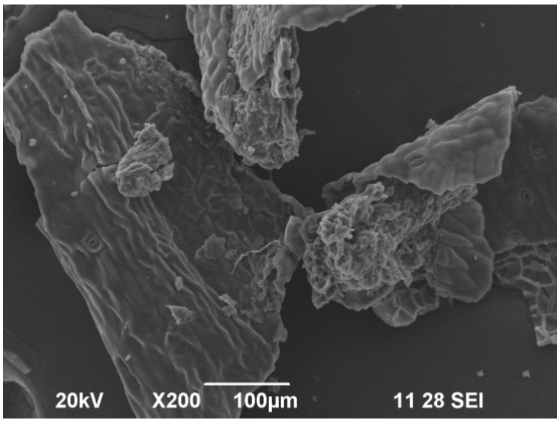
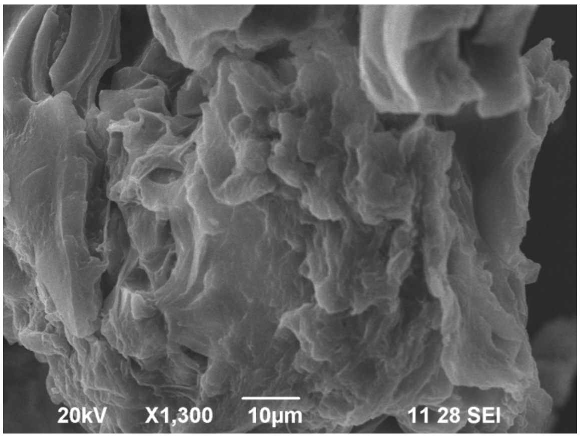


Fig. 5. SEM structure of PAN- Cu (II)



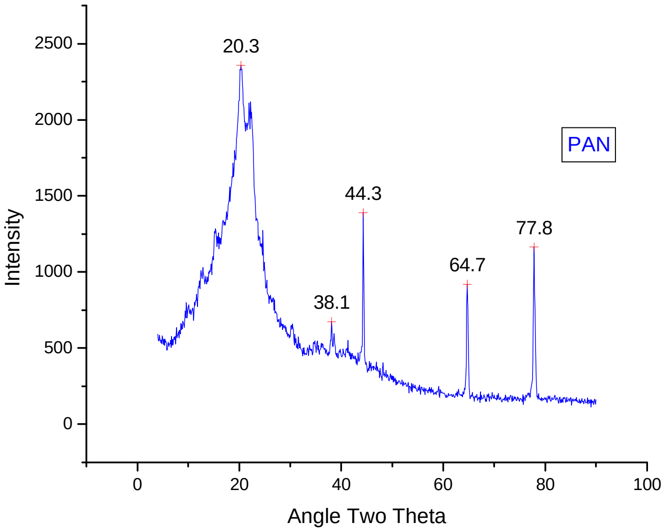


Fig. 6. XRD spectra of PAN

Batch mode studies

Effect of pH

The effect of initial pH value on adsorption percentage of metal onto PAN was examined over a range of pH values from 2 to 10 and the results are presented in Fig.7. As elucidated in Fig.7. the metal removal was at its minimum at the initial pH 2. In Nickel aqueous solution, adsorption capacity increased up to pH 5.0 and then decreased slightly and then increased. The increase in the amount adsorbed as pH increased from 2.0 to 7.0 may be because of the presence of negative charge on the surface of the adsorbent, which may be responsible for metal binding. However, as the pH is reduced, hydrogen ions compete with the metal ions for the sorption sites; the overall surface charge on the adsorbent becomes positive and hinders binding of positively charged metal ions. The increase in the removal of Ni (II) ions took place after pH 7 may be due to precipitation of metal ions in alkaline medium and not by adsorption [23].

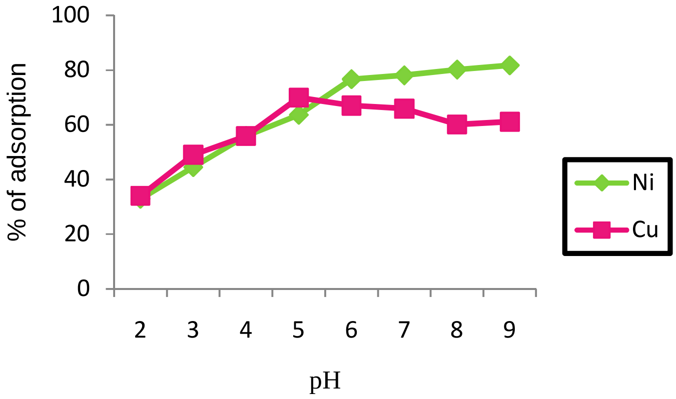


Fig. 7. Effect of pH on biosorption for Ni (II) and Cu (II) onto PAN

In copper aqueous solution, as the pH solution increased from 2 to 9, the Cu (II) metal ions adsorbed increased from pH 2 to 6, and then increased to certain extent and remained constant. The increase in the amount adsorbed as pH increased from 2.0 to 7.0 may be because of the presence of negative charge on the surface of the adsorbent, which may be responsible for metal binding. However, as the pH is reduced, hydrogen ions compete with the metal ions for the sorption sites; the overall surface charge on the adsorbent becomes positive and hinders binding of positively charged metal ions [24]. At pH 6.0, precipitation of insoluble metal hydroxides occurs, restricting true adsorption studies [25].

Effect of initial metal concentration

The influence of metal concentration on adsorption of nickel and copper are shown in Fig.8 when the metal concentration was increased from 25 to 200 mg/L, the percentage of Nickel adsorbed decreases from 90.12% to 62.8% where as for copper it increases from 69.9 to 73.5 from 25 ppm to 200 ppm. These results show that the removal of copper and nickel are highly concentration dependent. As for the nickel ions, the percentage of adsorption decreases with the increase in ion concentration. It means that the adsorption is highly dependent on initial concentration of nickel ion. The reason behind this is at lower concentration, the ration of initial numbers of nickel ion to the variable surface area is low and subsequently the fractional adsorption becomes independent of initial concentration [26].

Metal uptake per unit weight of adsorbent increases with increasing initial metal ion concentration, is because at higher initial concentrations the ratio of initial number of moles of metal ions to the available adsorption surface area is high. This may be attributed to an increase in the driving force of the concentration gradient with increasing the initial metal concentration [27].

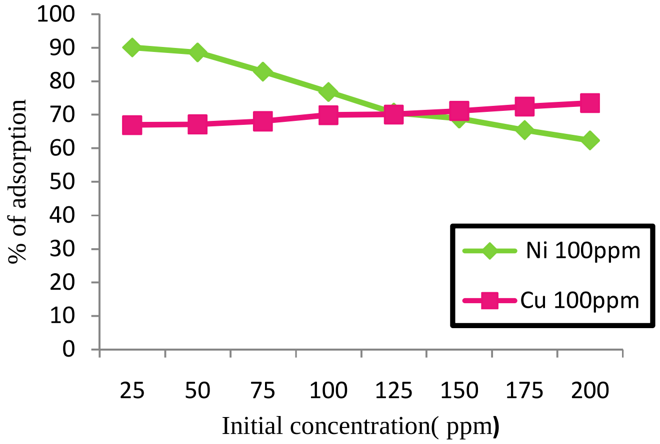


Fig. 8. Effect of initial metal concentration for Ni (II) and Cu (II) onto PAN

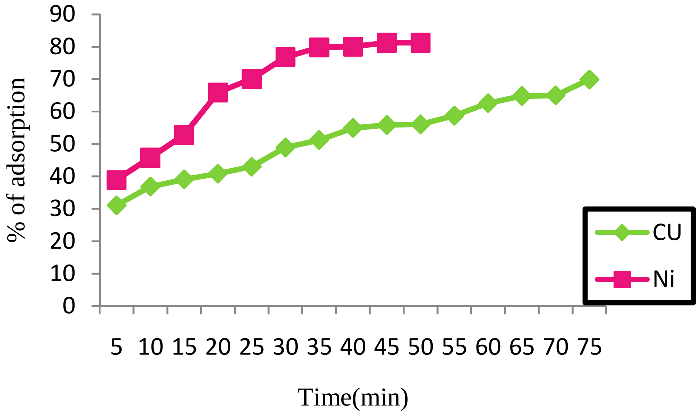


Fig. 9. Effect of contact time for Ni (II) and Cu (II) onto PAN

Effect of contact time on adsorption

Agitation time was evaluated as one of the most important factors affecting adsorption efficiency. The optimum time for nickel removal was 50 minutes and copper was 75 minutes for the adsorption of PAN Fig.9. These experimental studies showed that highly efficient adsorption of nickel as well as copper can be achieved rapidly. The equilibrium was attained after shaking for 50 minutes for Ni (II) and 75 min. for Cu (II). Therefore in each experiment the shaking period was selected as 50 min for nickel and 75 min. for copper. As seen in Fig.9. Ni (II) exhibited a greater affinity than Cu (II) ions.

Effect of Adsorbent Dose

The adsorption of the metal on carbon was studied by varying the concentration of the *Acacia nilotica* leaf biomass (0.2- 1 g mL^{-1}). The percentage of adsorption increased as the adsorbent concentration increased shown in Fig. 10. (Metal concentration: 100 mg L^{-1}; contact time: 1 h; pH: 6 and 5 for Ni (II) and Cu (II) respectively). The increase in the percent removal of metals with the increase in adsorbent dosage is due to the availability of larger surface area with more active functional groups. At equilibrium time 50 min and 75 min, the adsorption increases from for an increase in adsorbent dose from 0.2-1 g for Ni (II) and Cu (II) by PAN, respectively. The increase in percentage removal was due to the increase of the available sorption surface sites. A similar observation was previously reported from removal of Malachite Green dye from aqueous solution from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption [25].

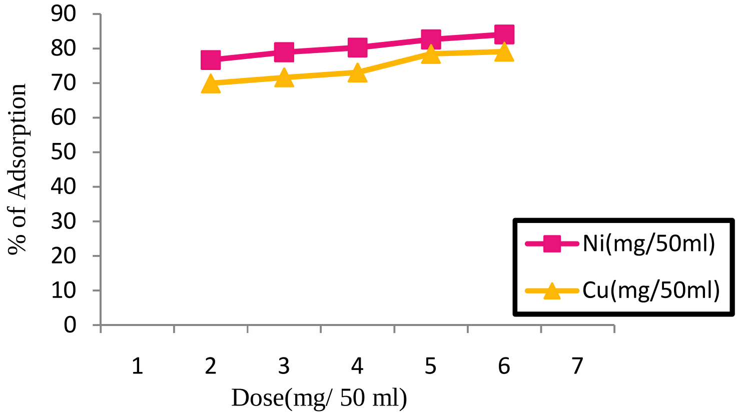


Fig. 10. Effect of adsorbent dose for Ni (II) and Cu (II) onto PAN

Adsorption isotherm

Adsorption isotherms describe the interaction of adsorbates with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism path-ways. Therefore, the correlation of equilibrium data by the empirical equations is essential to the practical design and operation of adsorption systems. The experimental data of nickel metal and copper metal were modeled using Langmuir, Freundlich and Temkin isotherm models. The adsorption data obtained by fitting the different isotherm models with the experimental data are listed in **Table 3**, with the linear regression coefficients, R^2. **Table 3** shows the values of the correlation coefficient (R^2), sorption capacity (Q_m), and sorption energy (n) calculated from the plot. The correlation coefficient (R^2) for the adsorption of nickel and copper onto PAN is equal to 0.975 and 0.978, showing a favorable adsorption of Ni (II) and Cu (II) onto PAN in single system (S). The value of Q_m obtained was equal to 20.64 mg/g and 21.80 mg/g for Ni (II) and Cu (II), indicating a very strong monolayer adsorption of the adsorbate on the surface.

The applicability of Langmuir isotherm model suggests that the adsorption takes place on homogeneous sites within the adsorption site (the adsorbed layer is one molecule in thickness; with each molecule possess constant enthalpies and sorption activation energy. The results also demonstrate there is no interaction and transmigration of metals in the plane of the neighboring surface.

Adsorption kinetics

The kinetics of adsorbate uptake is important for choosing optimum operating conditions for design purposes. In order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control and mass transport process, kinetic models have been used to test experimental data from the adsorption of Ni (II) and Cu (II) onto PAN. These kinetic models were analyzed using pseudo-first order [28], pseudo-second-orders [29] and Elovich equation [30].

Table 3 Adsorption isotherm data for adsorption of Ni (II) and Cu (II) ions by PAN

Isotherm	Variable	Ni(II)	Cu(II)
Langmuir	Q_m (mg g^{-1})	20.64	21.80
	b (L mg^{-1})	0.0251	0.0161
	R^2	0.998	0.992
	1/n	1.623	0.865
Freundlich	K_f (mg g^{-1})	2.053	3.614
	R^2	0.975	0.978
Temkin	α (L g^{-1})	0.0540	0.0643
	β (mg L^{-1})	5.6423	5.4136
	b	446.24	465.33
	R^2	0.977	0.869

Pseudo-first-order equation

The pseudo-first-order equation of Lagergren is generally expressed as follows:

$$\log(q_e - q_t) = log\ q_e - \frac{K_1}{2.303}t \qquad (8)$$

The values of qe and K_1 for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of log (q_e - q_t) versus time, respectively. The K_1 values, correlation coefficient values and qe values (experimental and calculated) are summarized in **Table 4**. The correlation coefficient for the pseudo-first-order model changed in the range of 0.922 and 0.913 for adsorption of nickel metal and copper metal ion onto PAN, respectively. Besides, the experimental q_e values did not agree with the calculated values obtained from the linear plots. It suggests that the kinetics of Ni (II) and Cu (II) adsorption onto PAN did not follow the pseudo-first-order kinetic model and hence was not a diffusion-controlled phenomenon.

Pseudo-second-order equation

The pseudo-second order equation is generally given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} \qquad (9)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K^2\, {q_e}^2 \qquad (10)$$

The K_2 and q_e values determined from the slopes and intercepts of the plot of t/qt are presented in **Table 4** along with the corresponding correlation coefficients. This is more likely to predict the behavior over the whole range of adsorption. The corresponding correlation coefficients (R^2) values for the pseudo-second-order kinetic model were greater than 0.997 for all both metals indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption of Ni (II) and Cu (II) onto PAN.

Simplified Elovich model

The simplified Elovich equations:

$$q_e = \frac{1}{\beta \ln{(\alpha\beta)}} + \frac{1}{\beta \ln t} \qquad (11)$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate constant and β (g mg^{-1}) is related to the extent of surface coverage and the activation energy for chemisorptions The values of α and β can be calculated from the plot of qt against 1/ln t. If the Ni (II) ion and Cu (II) ion adsorption by PAN fits Elovich equation, a plot of qt versus ln t should yield a linear relationship with a slope and an intercept.

Desorption

Regeneration of the adsorbent may make the treatment more economical and feasible. Desorption helps to elucidate the mechanism of metal adsorption and recycling of the spent adsorbent and the metal. If the adsorbed metals can be desorbed using neutral pH water, then the attachment of the metal to the adsorbent is by weak bonds. The effects of pH on desorption of Ni (II) and Cu (II) is shown in Fig.11. When pH was varied from 2 to 9, the percentage desorption of both metals was found to be decreases from 75.01 to 31.50 and 67.9 to 21.84 respectively for nickel and copper. Further increase in the pH of the solution did not show any significant increase in the percentage of desorption. From the results, it can be concluded that the adsorption mechanism was complex and dominated by both physisorption and chemisorptions. Desorption of metals by aqueous solutions indicates that the metals were adsorbed onto the adsorbent through ion-exchange mechanisms [31].

Table 4 Comparison of kinetic models of Cu (II) and Ni (II) onto PAN

Model	Variables	Ni (II)	Cu (II)
Pseudo first-order model	k_1 (min^{-1})	0.142	0.069
	q_e (mg/g)	20.04	21.91
	R^2	0.922	0.614
Pseudo second-order model	k_2 (g/mg/min)	1.324	7.565
	q_e (mg/g)	180	100
	R^2	0.988	0.971
Simplified Elovich model	b	162	159.4
	A_E	0.002	0.001
	R^2	0.956	0.913

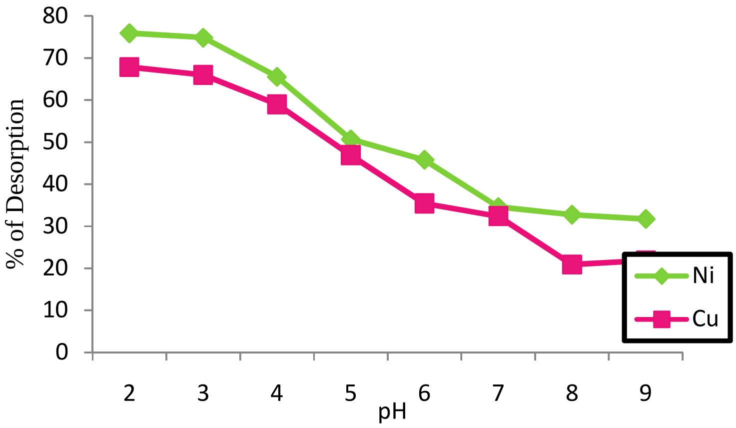


Fig. 11. Effect of pH on desorption of Ni (II) and Cu (II) on PAN

CONCLUSION

Result from this study confirmed that phosphoric activated *Acacia nilotica* (PAN) can be used as a suitable adsorbent for Ni (II) and Cu (II) ions from aqueous solutions as in terms on real industrial waste water. Adsorption of copper and nickel by PAN was highly dependent on the pH, PAN dosage, contact time and initial metal ions concentration. The adsorption data were well fitted by the Langmuir isotherm model; this is indicative of monolayer adsorption by PAN. Among the kinetic models tested, the adsorption kinetics for both metals was best described by the pseudo-second order equation. The *Acacia nilotica* leaves used in this work are freely and abundantly available. The data thus obtained could be employed as a low cost carbon as alternative to commercial activated carbon for the removal of heavy metal from waste water.

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