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Full Length Research Paper

Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr(VI) and Ni(II) from aqueous solution

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Heavy metals present in waste waters which are released into the environment by various industries have become a serious problem. This research is focused on the comparison of two agricultural wastes in the removal of Ni(II) and Cr(VI) ions from aqueous solution and the effect of HCl modification. The effects of adsorbent dose, initial concentration, contact time, pH and temperature on adsorption were investigated. Generally, the result showed an increase in adsorption by Cr(VI) with increase in mass of adsorbent with the exception of coconut husk which consistently had an adsorption of 96 ± 3% irrespective of the adsorbent loading. The coconut husk adsorbents(unmodified coconut husk 83 ± 3 and 81.4 ± 4.7%, HCl modified coconut husk 96 ± 4 and 24.1 ± 4% were found to be more efficient for Cr(VI) and Ni(II) respectively than teak tree bark adsorbents(unmodified teak tree 61.5 ± 3 and 80.9 ± 2.2%, HCl modified teak tree 81.9 ± 2.5 and 29.9 ± 2.6%). HCl modified adsorbents were found to better adsorbents for Cr(VI) ion while the unmodified adsorbents were better adsorbent for Ni(II) ion for all the parameters studied. The data for the adsorption of Cr (VI) and Ni(II) was tested with Freundlich adsorption isotherm model and it was found to be suitable for the adsorption of Cr(VI) and Ni(II) for both coconut husk and teak tree bark. The kinetic study of the adsorption process showed that adsorption of Cr(VI) and Ni(II) or both coconut husk and teak tree bark was found to follow the second-order.

Key words: Agricultural wastes, adsorption, heavy metals, adsorbents, aqueous solution.

INTRODUCTION

Industrial activities such as mining, electroplating, tanning, metallurgical operation and manufacturing have led to the release of heavy metals into the environment (Samara, 2006). Unlike the organic pollutants which are bio-degradable, heavy metal like Ni(II) and Cr(VI) are not bio-degradable (Rotterdamsewag, 2006), thus, making them a source of great concern. Heavy metals bio-accumulate in living organisms reaching levels that cause toxicological effects (Samara, 2006). Human health, agricultural development and the ecosystems are all at risk unless water and land systems are effectively managed (Rao et al., 2002). In the environment, chromium exists in two stable forms which are the + III and the + VI states. While chromium (III) is known to be an essential trace element in plants and animal metabolism, the chromium (VI) is toxic, carcinogenic and mutagenic (Igwe et al., 2005). Nickel toxicity has been reported to cause pulmonary fibrosis and inhibit many enzymatic functions (Liphadzi and Kirkham, 2005). As a result of the toxicological effects of these metals, interest in heavy metal removal from waste water has been on the rise.

Some methods have been developed to remove heavy metals from waste water before discharge into the water bodies. These methods include reduction, precipitation, ion exchange reverse osmosis, dialysis and adsorption by coated carbon. Most of these methods are expensive so are not affordable for a developing country like Nigeria. They also have limited application as they cannot remove metals at low concentration (Faur-Brasquet et al., 2002). This has therefore led to the use of agricultural wastes in removal of heavy metals. Agricultural wastes are characterized by ready availability, affordability, eco-friendliness 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

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(Olayinka et al., 2007).

Peanut hull (an agricultural waste) was found to be 36 times more efficient compared to granular activated carbon which is the widely used adsorbent (Perisamy and Namasivayan, 1995). Other agricultural wastes which have been investigated for their metal adsorption property include sugar cane bagasse, soybeans hulls, cotton seed hull, rice bran, rice husk and straw as efficient heavy metal adsorbents (Nasim et al., 2004). Waste tea, coconut shell, coconut husk and teak tree bark which are all agricultural wastes were also found to be efficient metal adsorbents. Adsorption of Cr(VI) and Ni(II) were pH dependent, contact time dependent and adsorbent loading dependent (Olayinka et al., 2005; Olayinka et al., 2007). Activated Amarind (*Tamarindus indica)* seeds using sodium biocarbonate and HCl activated neem leaves were found to be efficient adsorbent for Cr(VI) (Babu and Gupta, 2008, 2009). It was also found that sodium hydroxide modification of oat and wheat straws improved adsorption of heavy metal for oat straw biomass but did not improve that of wheat straw biomass. However both the modified and unmodified were good enough to remediate heavy metals (Rios et al., 1999).

Previous researches have shown teak tree back and coconut husk to be good adsorbent due to their high lignin content (Olayinka and Adu, 2005; Olayinka et al., 2005). The coconut husk, a waste in the agricultural sector is a low cost adsorbent for heavy metal but has found use in the furniture industry for making foot mats, in the traditional medicine sector as medicine for treating fever in children and for making fire for cooking in local settings. Teak tree bark a waste obtained from the timber industry in Nigeria is only used in making fire for cooking. Hence a comparison of their adsorptive properties if in favor of the teak tree bark will lead to a conservation of the coconut husk and increase the use of teak tree back as its economic value is less.

The aim of this study was to compare the use of modified coconut husk and teak tree bark in the removal of Ni(II) and Cr(VI) from aqueous solution. The research involved the modification of both teak tree bark and coconut husk with HCl and investigation of some experimental conditions such as pH of solution, contact time, adsorbent loading and temperature as it relates to adsorption of the metal to the adsorbents. It also involved the use of Freunlich adsorption isotherm model to fit in the data. Kinetic study using pseudo – first order and second – order kinetic model were also used to investigate the mechanism of adsorption.

MATERIALS AND METHODS

Adsorbents

The adsorbents were prepared as described by Hanafiah et al. (2006). Each of the adsorbents (coconut husk and teak tree bark) were cut into small pieces and blended. They were washed with distilled water to remove dirt and colour and air- dried for 24 h to avoid thermal deactivation of the adsorbent surface respectively. They were sieved to pass through a 2 mm stainless steel sieve and a portion of each of the adsorbent was stored in clean polyethylene containers (labeled as unmodified adsorbent) prior to analysis. For the modification of the adsorbents, about 400 g of each of the washed adsorbents were mixed with 600 ml of 0.1 mol dm^{-3} HCl. The mixture was heated at 120˚C for 30 min with occasional stirring. Each of the adsorbent was separated from water using Buckner funnel and a vacuum pump and washed with distilled water until the washings were free of color and the pH of wash solution was about 7. The washed adsorbents were air-dried for 24 h and labeled as HCl - modified coconut husk and HCl- modified teak tree bark respectively.

The concentration of Cr(VI) and Ni(II) in each of the adsorbent was determined by soaking 1 g of the adsorbent in 10 ml de-ionized water for one hour with continuous agitation, after which it was centrifuged at 2000 rpm with a Remi R-8C laboratory centrifuge. The supernatant was carefully decanted into acid cleaned polyethylene containers and analyzed using a Flame Atomic Absorption Spectrophotometer (FAAS) Perkin Elmer A Analyst 200. The pH of the adsorbents used (modified and unmodified) was determined according to British Standard ISO 10390 (2005), using a Mettler Toledo pH meter.

The cation exchange capacity of the adsorbent was determined by saturating the adsorbing site of 50 g adsorbent with 33 ml of 1 M sodium acetate. The exchangeable sodium ions were removed by washing the saturated adsorbent with 95% ethanol. 33 ml of 1 M solution of sodium acetate was used to wash the adsorbent three times and the supernatants of each wash were kept in a volumetric flask and made up to the mark with distilled water. The sodium content was determined using a flame atomic absorption spectroscopy with cesium chloride used as an ionization suppressant.

The surface area of the coconut husk and teak tree bark adsorbents were determined by iodine adsorption method (Akporhonor et al., 2007). The amount of iodine absorbed from aqueous solution was estimated by titrating a blank with standard thiosulphate solution and compared with titrating against iodine containing the sample coconut husk and teak tree bark respectively. Indicator used was starch. The surface area was calculated as follows.

$$\text{Surface area (mg/g)} = \frac{V_{\text{blank}} - V_{\text{blank}} \times V\,M \times 126.91}{V_{\text{blank}} \times W}$$

Where;

V_{blank} = Volume of blank used.
V_{sample}= Volume containing adsorbent.
M = Molarity of iodine.
W = Weight of adsorbent used.

Adsorbates

The solutions of Cr(VI) and Ni(II) metal ions were prepared from analytical grade $K_2Cr_2O_7$ and $NiCl_2$ respectively. For the preparation of 1000 mgl^{-1} solutions of each of Cr(VI) and Ni(II), 2.8234 g of $K_2Cr_2O_7$ and 4.782 g of $NiCl_2$ respectively were dissolved in de-ionized distilled water and made up to 1000 ml in standard flasks. The prepared aqueous solutions (1, 000 mg/L) (stock solutions) were diluted with de-ionized water to obtain the working standard solutions. The main characteristics of these ions are summarized in Table 1.

Adsorption experiments

For the adsorption experiment, the effect of adsorbent loading on the adsorption of the ions was investigated. Between 0.2 - 1.0 g of the adsorbent was weighed respectively into conical flasks. 20 ml of 10 mg/l solution of each of the metal ion solution was added and

Table 1. Main characteristics of metal ions studied.

Property	Cr(VI)	Ni(II)
Atomic weight ($gmol^{-1}$)	51.996	58.693
Formula	$K_2Cr_2O_7$	$NiCl_2.6H_2O$
Solubility @ 20°C (gcm^{-3})	11.50	2.54
Ionic radius	0.44	0.69
Pauling electronegativity	1.66	1.91

the mixture shaken with an IKA HS 260 basic reciprocating shaker at 150 rpm for 30 min. The mixtures were centrifuged at 2, 000 rpm for 30 min, the supernatant decanted and the metal ion content was determined using a Perkin Elmer AA Analyst 200 Flame AAS. The percentage adsorption was determined by;

$$\frac{C_o - C_a}{C_o} x100$$

Where; C_o = Initial concentration of solution, C_a = Concentration of the solution after adsorption.

In order to investigate the effect of concentration on the adsorption of metal ions, 0.4 g of the adsorbent was added into 20 ml each of varying concentrations (between 10 - 100 mg/L) of the metal ion solutions. The mixtures were shaken, centrifuged and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 0.4 g of the adsorbent to 20 ml of 10 mg/L and shaken using varying contact times (between 30 – 180 min) and the percentage of adsorbed ions determined. The effect of pH on adsorption of the ions was investigated using 0.4 g of the adsorbent and 20 ml of 10 mg/L and the pH of the solution was adjusted between 2 and 12. The mixture was shaken for 90 min, centrifuged and the amount of ion adsorbed was determined. The adsorbents used were unmodified teak tree bark, unmodified coconut husk. In order to investigate the effect of modifying the adsorbent, each of the experiments were repeated using, HCl - modified teak tree bark and HCl-modified coconut husk. For quality control, the experiments were performed in triplicates.

Adsorption isotherm models

The Freundlich adsorption isotherm models were used. The Freundlich isotherm (Feundlich, 1906) is expressed as

$N_e = K_f C_e^{1/n}$

Where; N_e = x/m (amount of metal ions per unit mass of adsorbent) when the equilibrium concentration is C_e.

To simplify the equation, it was linearized thus:

$\text{Log } N_e = \text{Log } K_f + 1/n\text{Log } C_e$.

The Freundlich Isotherm Coefficients were determined by plotting $\text{Log}N_e$ against Log C_e. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The constants indicate the adsorption capacity and the adsorption intensity.

Adsorption kinetics

The mechanism of the adsorption of Cr(VI) and Ni(II) was tested using pseudo first-order and second-order kinetic models.

Pseudo first-order kinetics

The non-linear form of pseudo first-order equation is given by:

$$\frac{dN_t}{dt} = k_{ad}(N_e - N_t)$$ (Ho and Mckay, 1999)

Where Ne and Nt are the amounts of each of Cr(VI) and Ni(II) adsorbed at equilibrium time and any instant of time (t) respectively. K_{ad} is the rate constant. The integrated rate law then becomes:

$$\log(N_e - N_e) = \log N_e - \frac{k_{ad}t}{2.303}$$

Plot of log(Ne-Nt) vs. t gives a straight line and the adsorption rate constant k_{ad} can be computed.

Second-order kinetics

Applicability of the second order kinetics is tested with the rate equation:

$$\frac{dN_t}{dt} = k_2(N_e - N_t)^2$$

Where; k_2 is the second order rate constant. From the boundary conditions t = 0 to t = t and $N_t = 0$ to $N_t = N_t$, the integrated rate law becomes:

$$\frac{1}{(N_e - N_t)} = \frac{1}{N_e} + k_2 t$$ and this can be rewritten as:

$$\frac{t}{N_t} = \frac{1}{h} + \left(\frac{1}{N_e}\right)t$$

Where; h = is the initial sorption rate as t $\rightarrow 0$. The plot of t/N_t = gives a linear relationship and N_e, k_2 and h. (Ho and Mckay, 1999, Gupta and Babu, 2009)

RESULTS AND DISCUSSION

Physicochemical properties of Adsorbents

Selected characteristics of the adsorbents were investigated and are presented in Table 2. The adsorbents were slightly acidic for HCl – modified adsorbents and neutral for unmodified adsorbent. For most applications, pH of 6 - 8 is thought to be acceptable (Akporhonor and Egwaikhide, 2007). Large surface area is a general requirement for good adsorbents. Surface area is a single most important characteristic of activated carbon designed

Table 2. Physicochemical characteristics of the adsorbents.

Parameters	Teak tree bark	Coconut husk
pH HCl Modified adsorbent	6	6
pH Unmodified adsorbent	7	7
Cation exchange capacity(CEC)(Meq/100g)	2.824	20.31
Heavy metal content (Cr(VI))	Not detected	Not detected
Heavy metal Content (Ni)	Not detected	Not detected
Surface area (m^2/g)	17.45	20.31

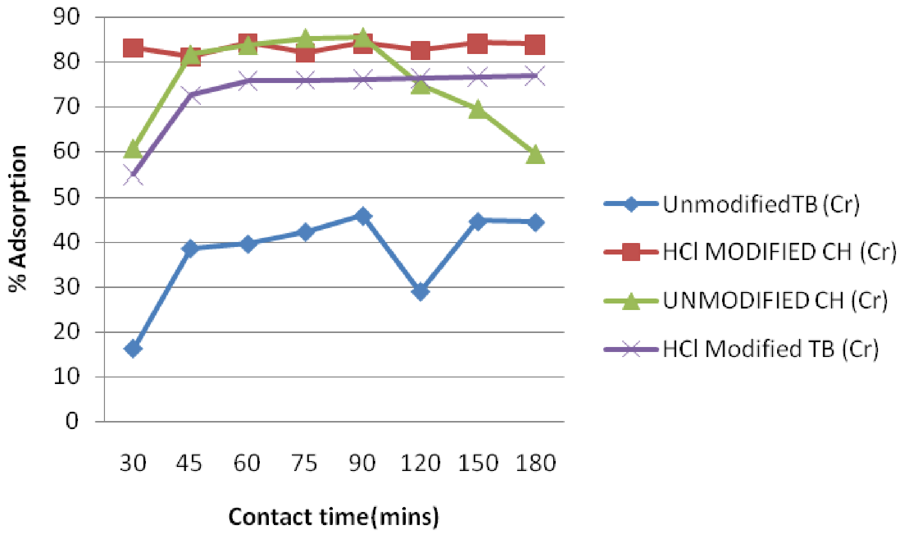

Figure 1a. Effect of contact time on adsorption of chromium ion.

for adsorption of compounds from liquid media (Akporhonor and Egwaikhide, 2007). The surface area of coconut husk was found to be larger (20.31 mg^2/g) compared to that of teak tree bark (17.45 m^2/g).

Ni(II) and Cr(VI) content were not detected in the two adsorbents which meant that these adsorbents had little or no Ni(II) and Cr(VI) contained in them to exaggerate the results. The cation exchange capacity was found to be 2.824 meq/100 g.

Effect of contact time on the adsorption of metal ions

The results for the effect of contact time on adsorption of Cr(VI) and Ni(II) are shown in Figures 1a and b. A pH of 3 was used for Cr(VI) solution while pH 7 was used for Ni(II) solution. The coconut husk adsorbents gave better percent adsorption than the teak tree bark adsorbents as the contact time increased. It was observed that, the HCl-modified coconut husk consistently had a constant percentage adsorption (95%) for chromium all through the contact times used which meant equilibrium was rapidly reached and as quickly as 30 min the adsorption sites where already saturated to maximum uptake capacity. This makes it the most efficient adsorbent of the adsorbents used in this research for Cr(VI) adsorption. For HCl-modified teak tree there was an initial increase in percentage adsorption but after 45 min contact time the percentage adsorption remained constant (54%). This might be due to saturation of the adsorption sites after 45 min after which little or no increase in percentage adsorption was observed as contact time increased. For unmodified coconut husk, the percentage of chromium adsorbed increased till 90 min after which there was a significant decrease in percentage adsorption. This could be as a result of desorption of the metal ions, while the unmodified teak tree had the lowest percentage adsorption of all the adsorbent used for Cr(VI) adsorption even though the percentage adsorption increased as contact time increased.

In the case of Ni(II), the percentage adsorption was constant for the coconut husk adsorbents while there were slight variation for the teak tree bark adsorbents. The unmodified and HCl modified coconut husk adsorbents consistently gave 96 and 50% adsorption respectively. It could be said that the metal uptake was rapid and the adsorbents were capable of adsorbing metals rapidly within 30 min, while for the teak tree bark

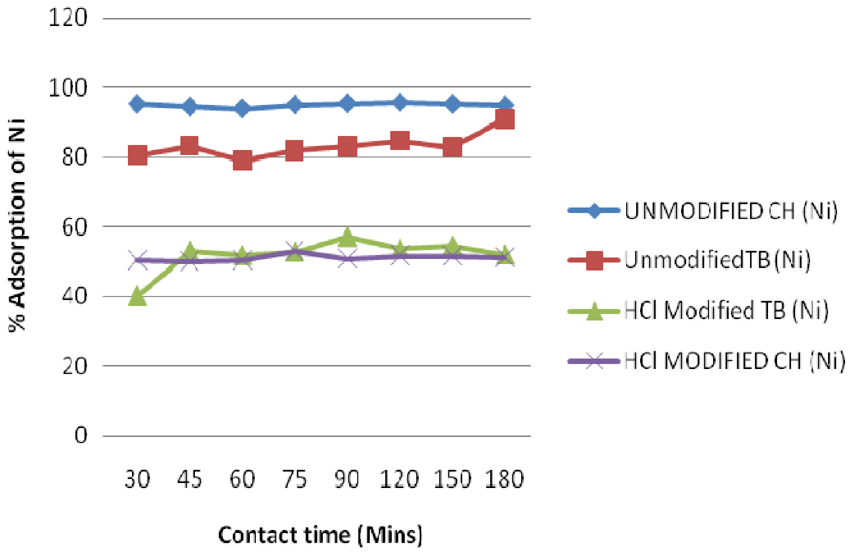

Figure 1b. Effect of contact time on adsorption of nickel ion.

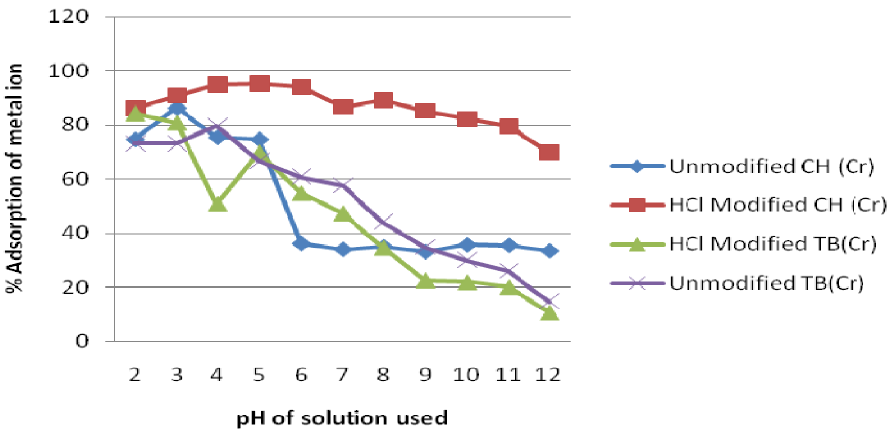

Figure 2a. Effect of pH on adsorption of metal ion.

their percentage adsorption increased with time. For the HCl-modified teak bark, the adsorption within the first 45 min was rapid and after which subsequent increase was slow. A similar trend was observed with the unmodified teak tree bark as it rapidly adsorbed the Ni(II) within the 30 min contact time.

Effect of pH on the adsorption of metal ion

The adsorption capacity of the adsorbents as a function of hydrogen ion concentration (pH) was determined. The results for the adsorption of Cr(VI) and Ni(II) are shown in Figures 2a and b. The uptake of heavy metal is pH dependent as seen in the Figures 2a and b. This could be because pH affects the solubility of metals in solution and the ions on the functional groups of the adsorbent (Malik and Ramest, 2007). Chromium adsorption was high for all the adsorbents at low pH values of 2, 3, 4 and 5.The adsorption capacity of all the adsorbents for Cr(VI) decreased with increasing pH values, but for the HCl-modified adsorbent the decrease in percentage adsorption was slight. The decrease was obvious in the teak tree bark adsorbents. This is probably due to the lower surface area of teak tree bark as seen in Table 1, hence a lower number of adsorption sites as compared to the coconut husk. Generally, Cr(VI) is better adsorbed at low pH values. This could be because at low pH Cr(VI) exist as Cr^{3+} and can therefore be better adsorbed by the C = O functional group on the adsorbent since oxygen is electronegative and can attract ions that are positively charged (Sharma and Forster, 1994). Also according to Samanta et al. (2002), at low pH, there is presence of a large number of H^+ ions, which in turn neutralizes the

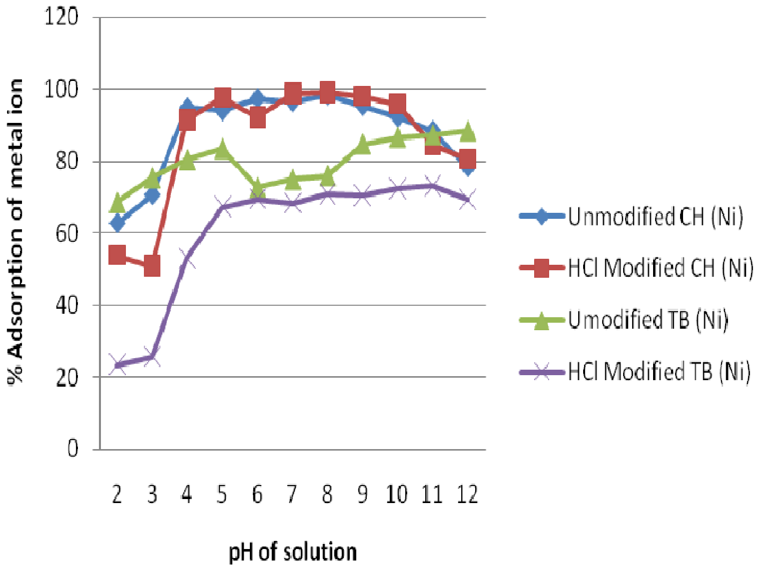

Figure 2b. Effect of pH on adsorption of Ni(II) ion.

negatively charged adsorbent surface by reducing the hin-drance to the diffusion of dichromate ions. The decrease in percentage adsorption of chromium at higher pH could be due to the high number of hydroxyl which causes hindrance to the diffusion of chromate ions (Olayinka et al., 2007).

The following reaction mechanism for adsorption of Cr(VI) at different pH is proposed by Bayat (2002).

$$2H^+ + 2HCrO^{4-} \overset{2H^+}{\longleftrightarrow} 2H_2CrO_4 \overset{2H^+}{\longleftrightarrow} 2H_2O + Cr_2O_2^{7-} \overset{2H^+}{\longleftrightarrow} 2CrO_3 + H_2O$$

At lower pH, dominant form of Cr(VI) is $HCrO^{4-}$ while the surface of adsorbent is charged positively. The H_2CrO_4 and CrO_3 exist as poly-nuclear species at high chromium concentration and at low pH value.

In the case of Ni(II), all the adsorbents had high adsorption of between 65 to 99% at pHs of 8 - 9. It is apparent that Ni(II) is strongly adsorbed at higher pH values. The optimum pH for the adsorbents could be said to be pH 7 and 8. This could be due to an increasing negative charge density on the adsorbent surface. At pH greater than 8, Ni(II) removal was mostly due to precipitation and not by sorption. A similar result was obtained when sawdust and other wastes were used as seen in Table 3.

Effect of adsorbent loading on the adsorption of Cr(VI) and Ni(II)

The result for the adsorption of Cr(VI) and Ni(II) is shown in Figures 3a and b respectively. For Cr(VI), HCl-modified coconut husk consistently removed almost 100% of the Cr(VI) from the synthetic effluent regardless of the adsorbent loading. This could be because the HCl- modified coconut husk has positively charged sites due to the acid and the Cr(VI) in solution exits as chromate ion which is negative. The presence of a higher number of adsorption sites on a small mass of the adsorbent probably accounts for the reason why variation in adsorbent loading had no effect since 0.2 g of adsorbent already removed about 100%. The higher number of adsorption sites on HCl-modified coconut husk compared to HCl-modified teak tree bark could probably be as a result of the higher surface area of the coconut husk. It was also observed that as adsorbent loading of the HCl-modified teak tree bark increased, adsorption increased. There was found to be a rise in adsorption from 15.9 to 81.9% as the mass of adsorbent was varied from 0.2 to 1 g. This may be attributed to increased surface area and availability of more adsorption sites. This is in agreement with the findings of Periasivayam et al. (1995).

The percentage adsorption of Cr(VI) by the unmodified coconut husk and unmodified teak tree bark increased with increasing adsorbent dosage. A similar trend was observed with unmodified teak bark. This is also attributed to increased surface area and the availability of more adsorption sites.

In the case of Ni(II), the unmodified adsorbents removed more Ni(II) compared to the HCl-modified adsorbents. The percentage of Ni(II) removed increased to 99.77% as the adsorbent loading of the unmodified coconut husk increased from 0.2 g to 0.6 g while a sharp decrease in adsorption was noticed at 0.8 g. This may be due to aggregation of adsorption sites resulting in decrease in total adsorbent surface area of particles available to Ni(II) and an increase in diffusion path length. The lower percentage of adsorption of both HCl-modified coconut husk and HCl-modified teak tree bark as

Table 3. Maximum adsorption capacity of various low cost adsorbents and agricultural waste (Gupta and Babu, 2009).

S/NO	Adsorbent	Maximum adsorbent capacity *q*m (mg g-1)	Optimum pH
1.	Activated neem leaves	62.97	2
2.	Activated Carbon (Filtrasorb-400)	57.7	-
3.	Sawdust	41.52	1.0
4.	Coconut husk fiber	29	2.05
5.	Tea factory waste	27.24	2.0
6.	Leaf Mould	25.9	2.5
7.	Pine needles	21.50	2.0
8.	Sugar beet pulp	17.2	2.0
9.	Palm pressed-fibers	15.0	2.0
10.	Maize cob	13.8	1.5
11.	Sugar cane bagasse	13.4	2.0
12.	Activated charcoal	12.87	2.0
13.	Activated tamarind seeds	.08	7.0
14.	Almond	10	2.0
15.	Polymer grafted sawdust	9.4	3.0
16.	Maple sawdust	8.2	4.0
17.	Activated alumina	7.44	2.0
18.	Cactus	7.08	2.0
19.	Biomass residual slurry	5.87	2.0
20.	Waste tea	1.55	-
21.	Walnut shell	1.33	-
22.	Rice husks	0.6	-
23.	Soya cake	0.28	1.0

CH; coconut husk, TB; teak tree bark.

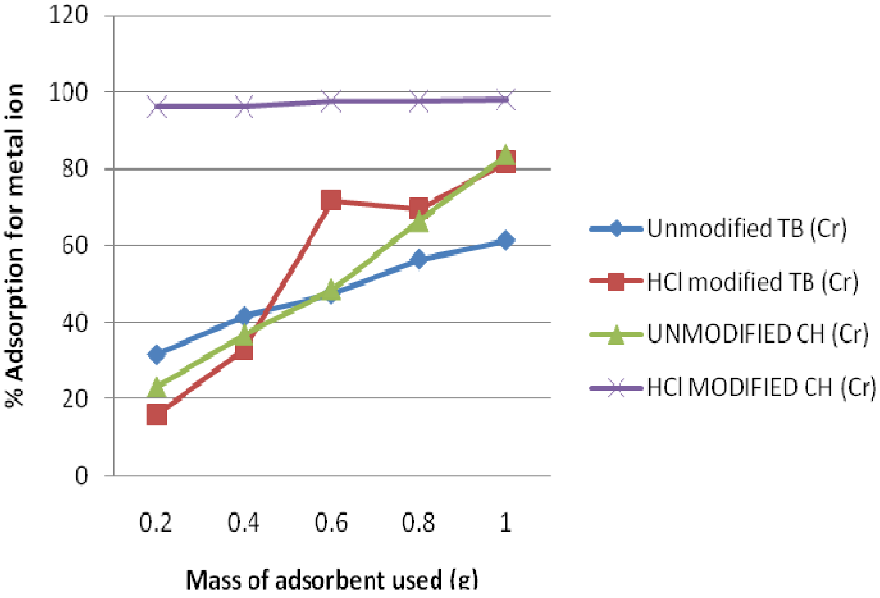

Figure 3a. Effect of adsorbent loading on Cr(VI) ion.

compared to the unmodified coconut husk and unmodified teak tree bark for Ni(II) could be as result of repulsion between the excess positive binding sites and Ni(II) ion which are positive in solution. The unmodified coconut husk gave a higher percentage adsorption when compared to the unmodified teak tree bark. This could be as

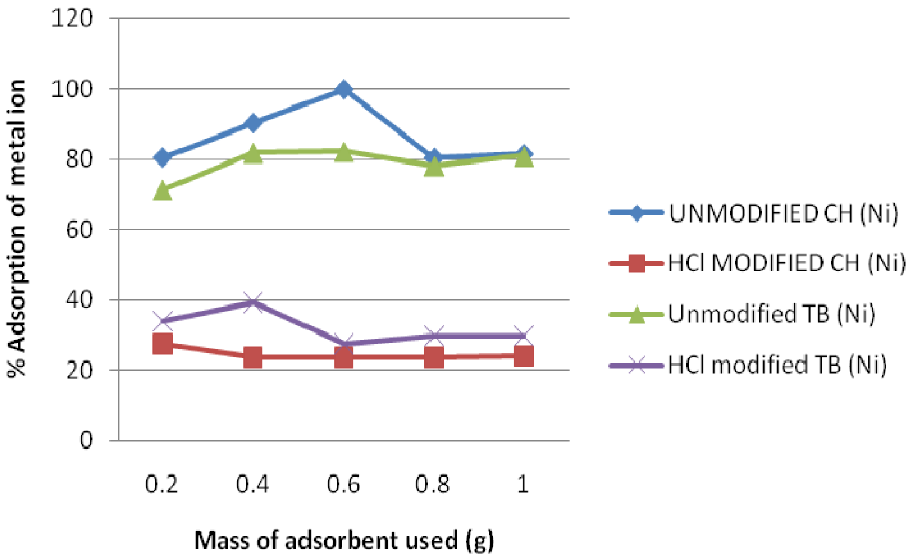

Figure 3b. Effect of adsorbent loading on Ni(II) ion.

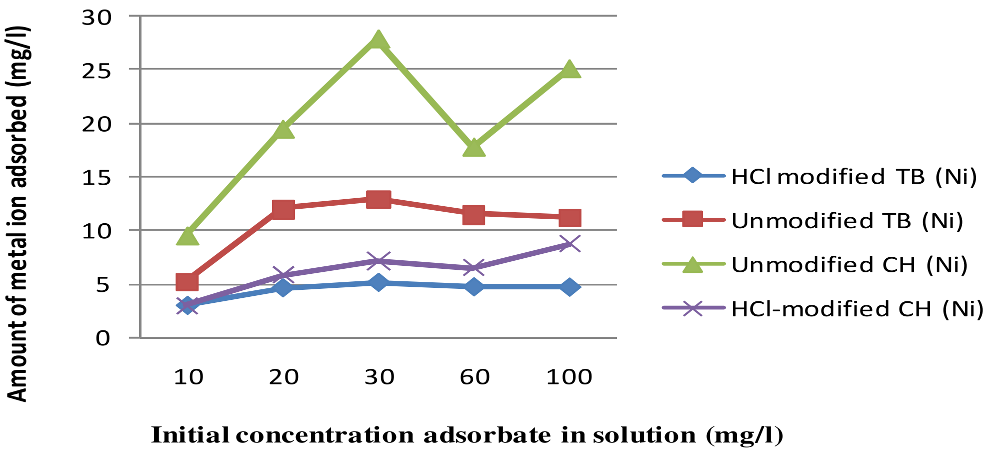

Figure 4a. Effect of initial concentration on adsorption of Ni(II) ion.

as a result of the higher surface area and CEC of the coconut husk as against the teak tree. The CEC of an adsorbent is a measure of the number of cations that 100 g of adsorbent can remove from solution. The CEC mechanism of removal of ions is based on ion exchange. Easily exchanged ions are displaced from their sites and replaced by bigger cations in solution which adsorb to these sites on the adsorbent. Ni(II) in solution exists as a cation and coconut husk with higher value of CEC exchanged more of it as against the teak tree bark.

The effect of concentration on the adsorption of the metal ions

The results of the effect of concentration on adsorption of Cr(VI) and Ni(II) to coconut husk and teak tree back are shown in Figure 4a and b. The HCl-modified coconut husk was found to have the highest adsorption of Cr(VI) .Generally, the adsorption of Cr(VI) by the adsorbents increased as the initial concentration of the Cr(VI) ion was increased. It was able to adsorb a concentration of 96 mg/L when an initial concentration of 100 mg/L solution of Cr(VI) ion was used. The high adsorption of the Cr(VI) by the HCl-modified coconut husk could be as a result of high surface area which means high adsorption number of adsorption sites.

Generally both the HCl-modified and unmodified teak tree bark had lower adsorption. This may probably be due to the tower surface area. In the case of Ni(II), the unmodified coconut husk had the highest concentration of Ni(II) adsorbed followed by the unmodified teak tree bark. The HCl had a lower concentration of Ni(II) removed. This is probably as a result of Ni(II) being posi-

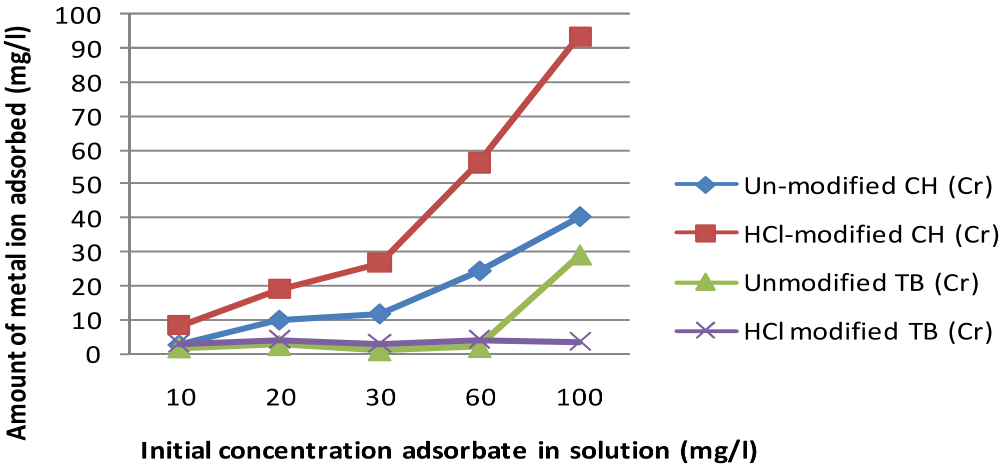

Figure 4b. Effect of initial concentration on adsorption of Cr(VI) ion

Table 4. Freundlich isotherm for the adsorbent on nickel and chromium adsorptions.

Adsorbent/metal in solution	Equation of graph	K_f	1/n	N	R^2
HCl modified TB/Cr	Y = 0.9255x + 0.9165	8.251	0.9255	1.0805	0.4117
Unmodified TB/Cr	Y = 0.0582x + 0.5392	3.461	0.0582	17.1821	0.5392
HCl modified TB/Ni	Y = 0.1631x + 0.6109	4.0823	0.1631	6.1313	0.4756
Unmodified TB /Ni	Y = 0.2658x + 0.3699	2.3437	0.2658	3.7622	0.4218
HCl modified CH/Cr	Y = 1.045x – 0.1120	0.2070	1.045	0.9569	0.9980
Unmodified CH/Cr	Y = 1.1269x – 1.6075	0.0247	1.1269	0.8874	0.9027
HCl modified CH/Ni	Y = 0.4005x – 0.0838	0.8245	0.4005	2.497	0.7767
Unmodified CH /Ni	Y = 0.3201x – 0.2110	0.6152	0.3201	3.124	0.4730

tively charged as compared to the negative chromate.

The amount of Ni(II) removed by some of the adsorbents was almost constant after certain points as the concentration of the initial solution increased from 10 - 100 mg/l. This probably indicated that at a concentration of 5, 8 and 12 mg/L of Ni(II) HCl modified teak tree bark, HCl modified coconut husk and unmodified teak tree bark respectively, the available binding sites had been saturated and the adsorbent could no longer bind further ions as the number of sites available on the adsorbent is constant. Furthermore, the presence of competing ion (H_3O^+) from the HCl modified adsorbent could also hinder the Ni(II) adsorbing capability of the adsorbent (Pandey et al., 2007).

Adsorption isotherm

The Freundlich Isotherm Coefficients were determined by plotting LogN_e against Log C_e and the results are shown in Table 4. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The constants indicate the adsorption capacity and the adsorption intensity. The linearity of the plot showed the representative nature of adsorption on the adsorbents tested. The correlation regression co-efficient showed that heavy metal adsorption was favorable. The values obtained were comparable to values obtained from the study of other adsorbents (Igwe et al., 2007). The teak tree bark had lower R^2 values and higher K_f than that of the coconut husk. This shows that the coconut husk is a better adsorbent for the metal ions.

Kinetic adsorption kinetics

The kinetic studies of adsorption of Cr(VI) and Ni(II) to teak tree bark and coconut husk was carried out using the first order and second order models on experimental data and the values obtained are as seen in Table 5. The regression coefficients obtained from the pseudo first order kinetic graph were low. This implies none applicability of the pseudo first order kinetic model to the experimental data of the adsorption of both Cr(VI) and Ni(II) to teak tree bark and coconut husk.

The second –order kinetic model kinetics was applied by plotting t/N_t vs. t gave high values of regression correlation co-efficient as seen in Table 4. This implied that the mechanism of adsorption of both ions on coconut husk and teak tree bark followed second order kinetics.

Table 5. Calculated kinetic parameters for second order kinetic model for the adsorption of Cr(VI) and Ni(II) using coconut and teak tree bark.

Adsorbent/metal in solution	Equation of graph	R^2
HCl modified TB/Cr	Y = 0.124x +0.8806	0.9962
Unmodified TB/Cr	Y =0.1970x + 6.2638	0.7634
HCl modified TB/Ni	Y = 0.1821x + 0.6349	0.9919
Unmodified TB /Ni	Y = 0.1099x + 0.8329	0.9936
HCl modified CH/Cr	Y = 0.1182x + 0.1206	0.9977
Unmodified CH/Cr	Y = 0.1669x -2.553	0.9602
HCl modified CH/Ni	Y = 0.1086x +4.448	0.2725
Unmodified CH /Ni	Y = 0.105x + 0.0188	0.9990

Conclusion

A comparison of two low cost adsorbents (Coconut husk and Teak tree bark) showed that coconut husk as an adsorbent was more efficient in metal ion removal from solution when compared with the teak tree bark as an adsorbent. This can be attributed to the large surface area and high CEC value of coconut husk. The coconut husk when modified with HCl was found to be the best adsorbent for Cr(VI) adsorption as Cr(VI) ion in solution exists as chromate ion which is a negative ion and easily exchanges for H^+ provided by the HCl while the unmodified coconut husk was the best adsorbent for Ni(II) ion adsorption. This was because the concentration of H^+ to compete with Ni(II) for the adsorption site were less compared to the HCl- modified adsorbents.

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