

BIOSORPTION OF COPPER (II) FROM AQUEOUS SOLUTION USING CITRUS SINENSIS PEEL AND WOOD SAWDUST: UTILIZATION IN PURIFICATION OF DRINKING AND WASTE WATER

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ABSTRACT

Excess of copper (>2 mg/L) in drinking water is significantly toxic to human being and ecological environments. Various treatment technologies for copper removal from industrial and municipal waste water effluents has been investigated in past. In the present study batch biosorption studies were carried out for the adsorption of Cu by using natural cheap agrowaste such as peel of Citrus sinensis and wood sawdust for the removal of Cu from aqueous solution. The effects of contact time, pH, concentration and dosage on the removal of Cu have been studied. Results indicated that contact time of 60 min is sufficient to achieve equilibrium at different concentrations. Determination of Cu was done using Atomic Absorption Spectroscopy and characterization of the agrowaste materials was done using FTIR. The peak percentage adsorption of Cu was attained at pH 6.5. Study reveals that peel of Citrus sinensis has good copper removal capacity than wood sawdust. peel of Citrus sinensis can reduce levels to 0.1ppm and wood sawdust can reduce copper up to 1.18 ppm which is less than permissible limit for copper in drinking water, i.e. 2ppm.

Keywords: *adsorption, removal efficiency, drinking water, waste waters, agrowaste materials, biosorbents.*

1. INTRODUCTION

There is a long history of human exposure to abnormally elevated levels of copper in food and drinking water, due to practices such as cooking in copper-lined or copper glazed pots and the supply of water through copper pipes. Copper rarely occurs naturally in water. Most copper contamination in drinking water happens in the water delivery system, as a result of corrosion of the copper pipes or fittings. Copper piping and fittings are widely used in household plumbing (Goyer *et al.*, 1991; Noggue *et al.*, 2000).

Water passing out of a mine contains large amount of copper, iron or other ores [4]. Industrial releases are only a fraction of the total environmental releases of copper and copper compounds. Other sources of copper release into the environment originate from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources e.g., windblown dust, volcanoes, decaying vegetation, forest fires, sea spray, etc [23]; [17]. Copper is both vital and toxic for many biological systems [48].

Immediate effects from drinking water which contains elevated levels of copper include vomiting, diarrhea, stomach cramps and nausea (Wisconsin Department of Natural Resources, 2003). Lowest observed adverse effect level (LOAEL) is 5.3 ppm [52]. In toxicity, copper can inhibit the enzyme dihydrophilhydratase which is involved in haemopoiesis and homeostasis. High copper levels in human liver has been reported to cause Wilson's disease, thalassemia, hemachromatosis, yellow atrophy of liver, tuberculosis and carcinomas. Women have more tendency of accumulating copper than men. Women also have more symptoms like Premenstrual syndrome, miscarriages, infertility, low libido related to copper imbalance [11].

Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies have been widely used to remove heavy metal ions from industrial wastewater [49]. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/Litre Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods [16].

Biosorption is the ability of certain inactive, dead microbial biomass for binding and concentration of heavy metals from aqueous solutions [32]. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. These biomass types can accumulate more than 25% of their dry weight in deposited heavy metals: Pb, Cd, U, Cu, Zn, Cr and others. Various metal-binding mechanisms have been postulated to be active in biosorption, such like chemisorption by ion exchange, complexation, coordination and/or chelation, physical adsorption, micro precipitation and oxidation/reduction. These mechanisms can also act simultaneously [27]. Biosorbents must be hard (to withstand pressure), porous, transparent to metal ion sorbate species, and have high

and fast sorption uptake even after repeated regeneration cycles [15]. Biomass material in granules form is more effective for adsorption of heavy metal because it provide more surface area. Sources of biomass include seaweeds, microorganisms (bacteria, fungi, yeast, and molds), Activated sludge, fermentation and industrial waste [27]; [5]. Biosorption can be carried out as a batch process, a continuous process, or a two-stage process with continuous metal recovery [27]. Biosorption is preferable because of limitation of other techniques.

Agro-wastes are now being used as adsorbents because of their abundant availability and low cost owing to their relatively high fixed carbon content and the presence of porous structure. Byproducts of agriculture or wood processing are cost-effective and environmentally-benign means to remove pollutants (heavy metals, hydrocarbons) and nutrients (nitrates, phosphates) from water [9]. One of the important agricultural wastes is the peel of different fruits, which can serve as potential adsorbents for the removal of diverse types of pollutants. Different types of fruits peels have been investigated for purpose of cleaning water. [34]; [2], [27], [10], [50], [3], [35], [6], [40], [25], [30], [35], [46].

In this research study, peel of citrus sinensis and wood sawdust have been used as biosorbent to remove copper (II) from solution. The aim of this research was to evaluate the efficiency of locally available cheap adsorbents; citrus sinensis and wood sawdust for Cu removal from aqueous solution. This research work will help us to design an economical technique for drinking water and waste water purification, contaminated by high copper concentration.

2. MATERIALS AND METHODS

Two cheap naturally available agro waste adsorbents citrus sinensis peel and wood sawdust were selected for the biosorption. Crude citrus sinensis peel were washed repeatedly with distilled water to remove dust and soluble impurities then dried for 72 hours in a convection oven at a temperature of 50°C. Dried citrus sinensis peels were crushed to fine powder and kept in plastic bottle for further use. Wood sawdust was commercially collected from furniture shop and washed with distilled water and dried in the sun. Then it was crushed and passed through a sieve of 30 mesh size. 1000ml of 1% phosphoric acid H_3PO_4 was added in 20g of wood sawdust. This mixture was heated for 20 minutes on Bunsen burner and then allowed to cool. It was filtered, washed with distilled water to remove any remaining acid and dried again. Activated samples were kept in plastic bottle for future use.

Characterization of biosorbents was done with help of Fourier-transform infrared spectrophotometer (SHIMAZU, FTIR-8400). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr. Characterization was done for both biosorbents before and after the biosorption process.

Stock copper solution (1000 mg/l) was prepared by dissolving 2.682 g of $CuCl_2 \cdot 3H_2O$ by Merck in a 1000 ml of distilled water. This stock solution was then diluted to specified concentrations. All chemicals were used of analytical reagent grade and purchased from Merck.

Adsorption studies were carried out by batch process. Biomass; citrus sinensis peel and wood sawdust were added to glass flasks containing a known amount of metal solution of the desired concentration. The mixture was stirred magnetically for 90 minutes, time more than sufficient to reach equilibrium. The pH of solutions was adjusted by adding dilute solutions of HNO_3 and NaOH. The bio-solids were then removed by filtration through Whatman filter paper (0.45 microns) and the filtrate was analysed for residual copper concentration by atomic adsorption spectrophotometer (Varian-220, Australia).

Metal uptake (q) was calculated using the general definition:

$$q = \frac{C_i - C_f}{C_i}$$

where C_i and C_f are the initial and final metal concentrations in solution (mg/l), respectively.

All experiments were performed in duplicate at least and mean values were presented with a maximum deviation of 5% in all the cases studied. Blank samples were run under similar experimental conditions but in the absence of adsorbent. It was not detected chemical precipitation and losses of copper to the containers wall.

Batch adsorption tests were conducted to study the effect of different parameters i.e.; pH, adsorbent dosage and time on removal efficiency of Copper by using wood sawdust and citrus sinensis peel.

Two batches of adsorption test were performed for wood sawdust and citrus sinensis peel. 0.5g of activated wood sawdust and citrus sinensis peel were added to 100ml of 100ppm Copper solution in conical flasks. Three different sets were prepared on the basis of pH values as pH 2, pH 4, and pH 6.5 and covered with aluminum foils. The effect of contact time was studied for 30, 60 and 90 minutes at constant initial copper concentration of 100ml. Thus the solutions were shaken for 30, 60, 90 minutes with digital shaker (Wise Shake SHO-2D, Witeg Germany). After required time intervals the suspension was filtered through filter paper (Whatman filter paper, mesh size: 0.45 microns). Each solution was filtered and the concentration of copper in the filtrate was measured by AAS (Varian-220, Australia). The instrument was calibrated with 10ppm, 50ppm and 90ppm copper solution and then samples were analyzed using AAS. A 0.5 g of biomass was added to glass flasks containing 100 ml of metal solution. The copper concentration was varied from 1 to 50 ppm, and contact time was kept at 90 minutes. Adsorption isotherms were obtained at pH 6.5.

3. RESULTS AND DISCUSSION

3.1 FTIR analysis

The FTIR spectrum of citrus sinensis peel and wood sawdust in Figure 1 shows number of adsorption peaks observed representing the complex nature of the material observed.

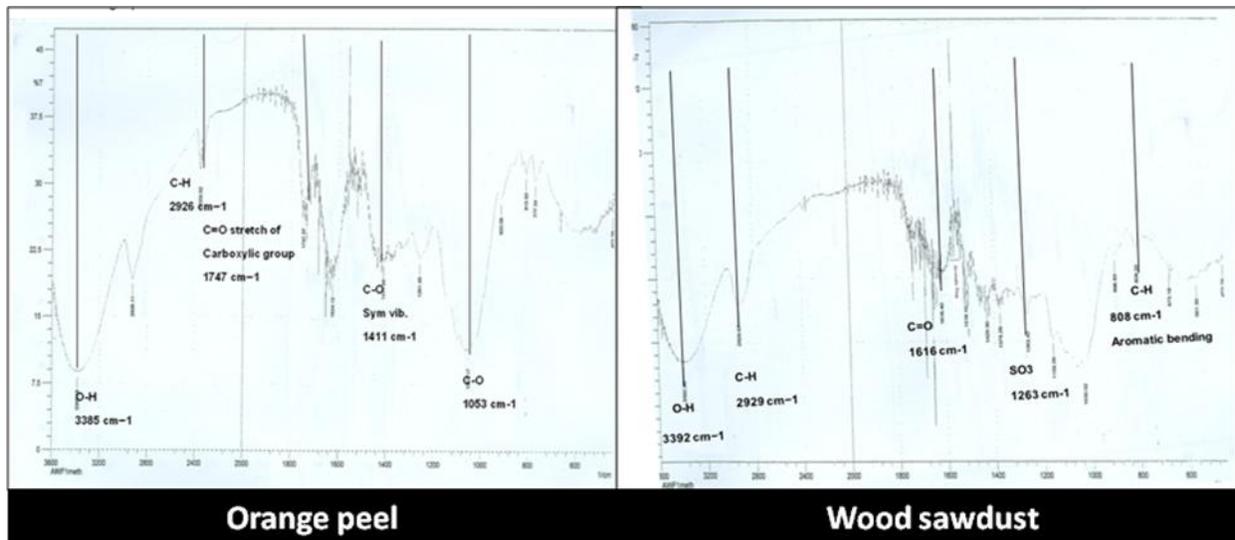


Figure 1 FTIR spectra of the orange peel and wood sawdust in KBr disk

In wood sawdust the broad, absorption peaks around 3392 cm^{-1} are indicative of the existence of hydroxyl groups which shows presence of phenols and alcohols. The peaks observed at 2935 cm^{-1} assigned to the C–H methyle and methylene groups. Absorbance at 1648 cm^{-1} and 1518 cm^{-1} shows presence of carboxylic groups; asymmetric and symmetric COO– offunctional groups of cellulose [13]. Peaks observed between 1280 and 1240 cm^{-1} indicative of stretching vibration of $-\text{SO}_3$ of hemicelluloses [33]. Peak at 1261 cm^{-1} may be assigned to deformation vibration of $\text{C}=\text{O}$ and stretching formation of $-\text{OH}$ of carboxylic acids and phenols [21].

In citrus sinensis peel sample absorption peaks around 3385 cm^{-1} can be assigned to O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin, thus, showing the presence of “free” hydroxyl groups on the adsorbent surface [19]. The peaks at 2926 cm^{-1} are attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids. The peak at 1747 cm^{-1} is due to stretching vibration of bond due to non-ionic carboxyl groups ($-\text{COOH}$, $-\text{COOCH}_3$), and may be assigned to carboxylic acids or their esters [21]. The peaks around 1647 cm^{-1} are due to the C–C stretching that can be attributed to the aromatic C–C bond. The peaks at 1624 and 1411 cm^{-1} are due to asymmetric and symmetric stretching vibrations of $\text{C}=\text{O}$ in ionic carboxylic groups ($-\text{COO}^-$), respectively [13]. Aliphatic acid group vibration at 1261 cm^{-1} may be attributed to deformation vibration of $\text{C}=\text{O}$ and stretching formation of $-\text{OH}$ of carboxylic acids and phenols. The strong band at 1053 cm^{-1} can be allocated to the C–O of alcohols and carboxylic acids [21]. The peaks found between 1130 – 1000 are due to Vibration of C–O–C, C–O–P and O–H of polysacchrides [47]. The functional group which is responsible for the binding of Cu will be discusses in the proceeding section.

3.2 Effect of pH

pH is a key controlling parameter in the bio-sorption process of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [49]. Effect of pH on copper removal is shown in Figure 2.

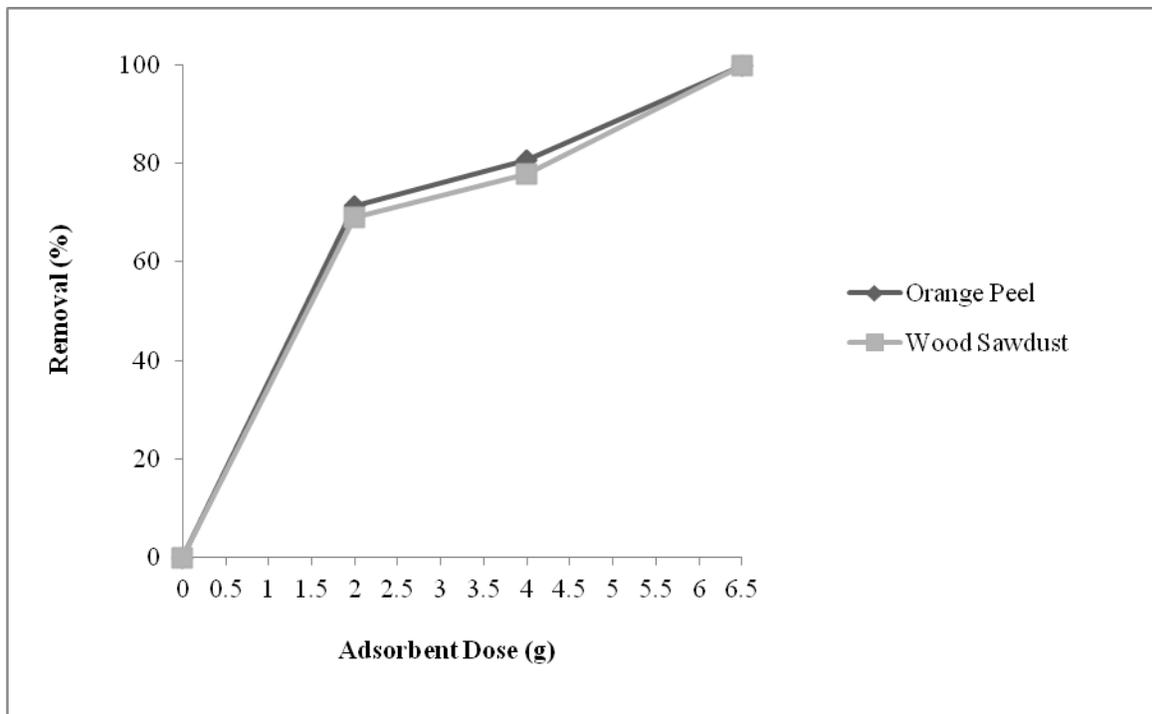
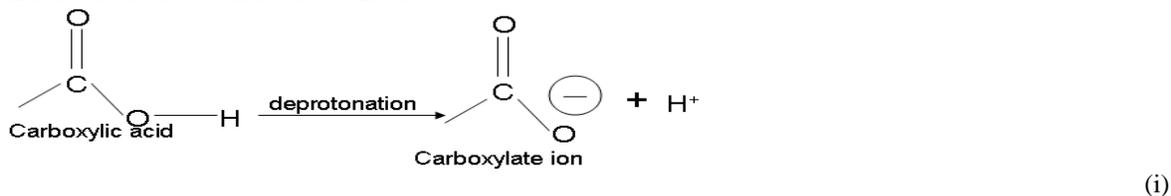


Figure 2. Effect of pH on the adsorption of copper by adsorbents

Bio-sorption was low at strong acidic medium and adsorption capacity increases with increasing pH values, until a certain pH value was reached. Bio-sorption increases between pH 2.0 and 6.5. A pH value of 6.5 was chosen as being the optimum for further experiment to avoid the precipitation of $\text{Cu}(\text{OH})_2$ as Cu^{2+} precipitates above pH 6.5 in the form of $\text{Cu}(\text{OH})_2$ and bio-sorption cannot occur [45].

At pH 6.5 there are three species present in solution. Cu^{2+} in very small quantity and $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ in large quantity [12]. The maximum bio-sorption efficiency is observed in the range of 2-6.5 may be due to the interaction of Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$ with surface functional groups present in the bio-sorbent. At pH 6.5 there are three species present in solution. These species are adsorbed at the surface of the biosorbent by two mechanisms; ion exchange and hydrogen bonding [22].

In citrus sinensis peel carboxylic group are active binding sites which cause the interaction with the copper. The carboxylic groups present in the adsorbent having the pKa values from 3 to 5. Therefore, at higher pH, deprotonation occurs as shown in equation (i) [12].

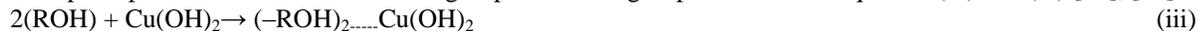


Carboxylate ion release and results in more interaction between the negatively charged carboxylate anions and positively charged copper species [22].

In wood sawdust phenolic compounds are active sites for bio-sorption mechanism. Based on structure of phenolic compounds ion exchange mechanism could be considered. Phenolic compounds have their high tendency to chelate metals. Phenolic compound possess hydroxyl and carboxyl groups, able to bind particularly copper [24]. A divalent heavy metal ion Cu^{2+} attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ion into solution as shown in equation Cu [8].



The preliminary look of FTIR shows inter- and intra-molecular hydrogen bonding of alcohols, carboxylic acids, and phenols showing the presence of “free” hydroxyl groups on the adsorbent surface [19]. Hydrogen bonding for the adsorption process is due to the $-\text{COOH}$ groups and $-\text{OH}$ groups as shown in equation (iii) and (iv) [12], [45].



R=Matrix of biosorbent

At low pH the H^+ ions compete with metal cations of Cu^{2+} for the exchange sites on the biosorbent, thereby partially releasing the cations which resulted in very low copper uptake. The heavy metal cations are completely released under circumstances of extreme acidic conditions. As the pH increases more ligands are exposed and the number of negatively charged groups on the adsorbent matrix probably increased and therefore electrostatic attraction between the cationic copper species and sawdust surface is likely to be increased [51], [31].

For making all solutions Deionized water was used. So it had zero charge and its pH was about 5.5 - 6. At pH below that zero charged Deionized water the surface charge of the adsorbents is positive which results in low copper sorption. At pH above zero charged Deionized water, the surface charge of the adsorbents is negative, and the Cu^{2+} ions in solution are attracted to the surface [28].

3.3 Effect of time

Contact time is a fundamental parameter in all transfer phenomena of bio-sorption. The adsorption kinetics was examined for better understanding of the dynamics of bio-sorption of Cu on to biosorbents like citrus sinensis peel and wood sawdust. To establish the equilibration time for maximum uptake of copper, the biosorption of copper on the biosorbents studied as a function of contact time. The results are shown in Figure 3.

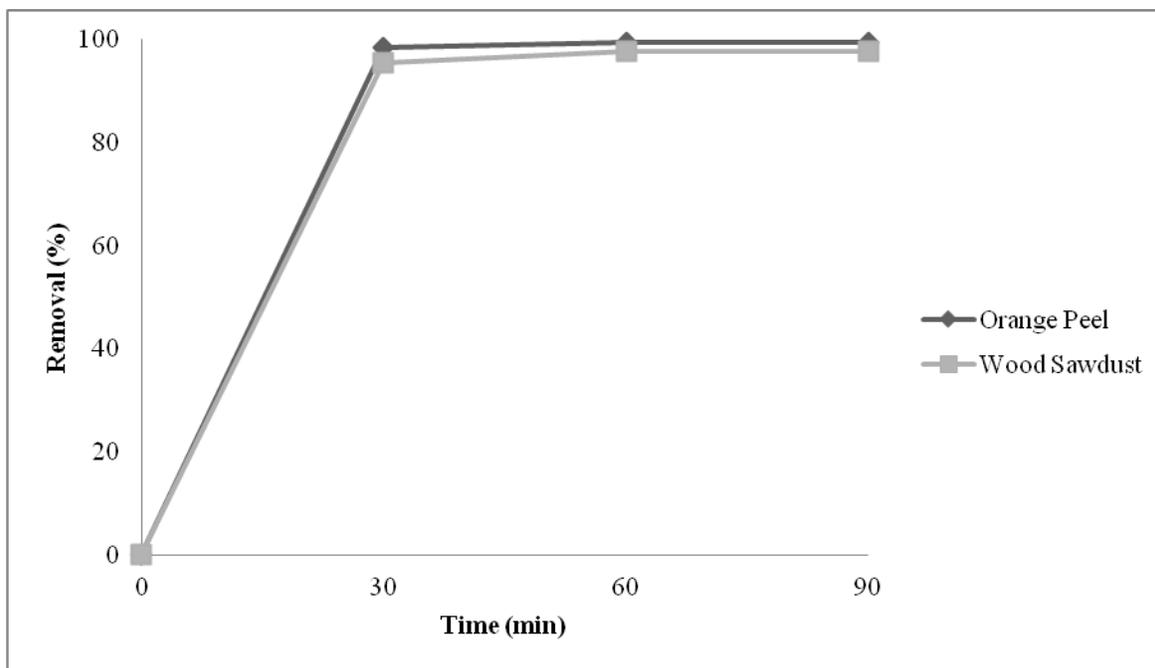


Figure 3. Effect of contact time on the adsorption of copper by adsorbents

It can be seen from the Figure 3 that rate of biosorption of copper was rapid at the beginning; removal of copper occurs from 100 ppm to 99.5 ppm for citrus sinensis peel and to 96.6 for wood sawdust after 30 minutes. It is evident from Figure 3 that rapid removal becomes slow after 30 minutes and become constant after 60 minutes.

Maximum biosorption occur in first 30 minutes. No change in residual copper concentration observed after 60 minutes indicates that the equilibrium is attained at 60 minutes for both biosorbents. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy [30]. The experiments were performed in a well-stirred batch system in which all the binding sites were readily available for metal uptake, and hence the effect of external film diffusion cannot be considered as a limiting step. Equilibrium attained in relatively short contact time indicates that the adsorption of copper is a chemical-reaction controlled, rather than diffusion controlled process [34].

There is no significant change in uptake of copper by the biosorbents after about 30 min although all the experiments were carried out up to 90 min. This is due to saturation of the adsorbents by the copper [22].

3.4 Analysis of the adsorption capacity by means of the Langmuir and Freundlich models

The study of the adsorption isotherm is fundamental, and plays an important role in determination of the maximal capacity of adsorbents. For the cases of adsorption on totally homogeneous surfaces, generally the Langmuir equation applies because here interactions between adsorbed molecules are negligible. The linear form of Langmuir isotherm is given below.

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max} C_e} + \frac{1}{q_{\max}} \quad 1$$

Where q_{\max} and K_L are langmuir parameters obtained from the slope and intercept of the plots respectively. q_{\max} is the maximum amount of adsorbate adsorbed per unit weight of adsorbent and K_L is the solute-adsorbent complex dissociation coefficient and shows the affinity between adsorbate and adsorbent.

The higher the value of q_{\max} shows higher adsorption capacity of the adsorbent. The value of q_{\max} for saw dust and citrus sinensis obtained from these plots are 31.25 and 14.75 respectively, showing that both the adsorbents are efficient in the adsorption of Cu(II). Similarly if the value of K_L is higher the affinity of that adsorbent for adsorbate will be higher. The value of K_L for the two adsorbents obtained from these plots is 0.21 and 0.687 for saw dust and citrus sinensis respectively.

While describing the adsorption in aqueous systems the equation of Freundlich applies fairly well. The linear form of Freundlich isotherm is given as.

$$q_e = K_F \times C_e^{1/n} \quad 2$$

Where C_e is the final Cu(II) concentration and q_e is the amount of Cu(II) adsorbed per unit weight of the adsorbent. K_F and n are Freundlich constants and are related to adsorption capacity and adsorption energy respectively. The logarithmic form of equation 1 is as follows.

$$\log q_e = \log K + \left(\frac{1}{n} \times \log C_e \right) \quad 3$$

The plot of $\log q_e$ vs $\log C_e$ give a straight line with slope equal to $1/n$ and intercept equals to K_F . The plots are given in the Figure 4.

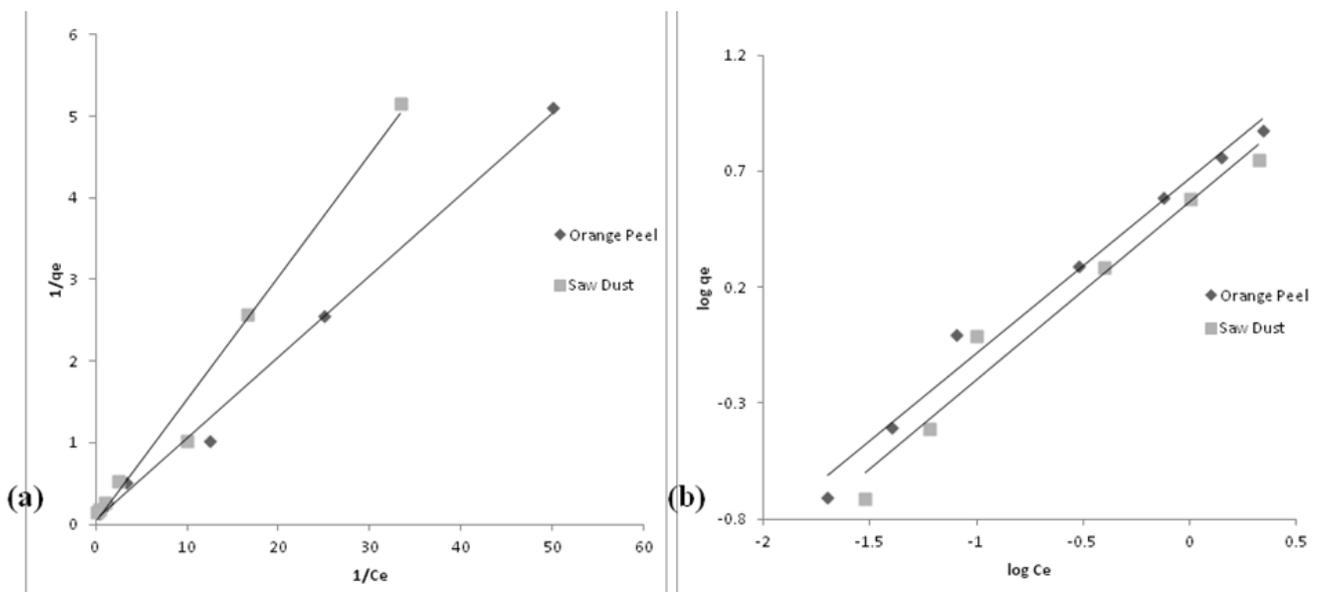


Figure 4 (a) Langmuir and (b) Freundlich isotherm for saw-dust and Orange peel

K_F is the adsorption capacity of the adsorbent, larger the value of K_F shows a greater overall capacity of the adsorbent. The value of K_F for both saw-dust and Citrus sinensis obtained for the plots are 3.7mg/g and 4.6mg/g respectively, showing a large adsorption capacity of both the adsorbent for Cu (II). Similarly value of n between 1

and 10 shows a favourable adsorption. From the plots the value of n for both the adsorbent obtained were 1.3 for saw dust and 1.33 for citrus sinensis, showing that adsorption process is a favorable one with both the adsorbent

3.5 Adsorption Kinetics

To find the mechanism controlling the adsorption process, pseudo-second order kinetics model was used to check the experimental data. The pseudo-second order kinetics rate equation is given as follows [43];

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad 5$$

While k_2 is the pseudo-second order rate constant (g/mg. min). At boundary conditions ($t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$), pseudo-second order kinetics model takes the following form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} \quad 6$$

The linear plot of t/q_t vs t give the pseudo-second order kinetics plots, as shown in Figure 5.

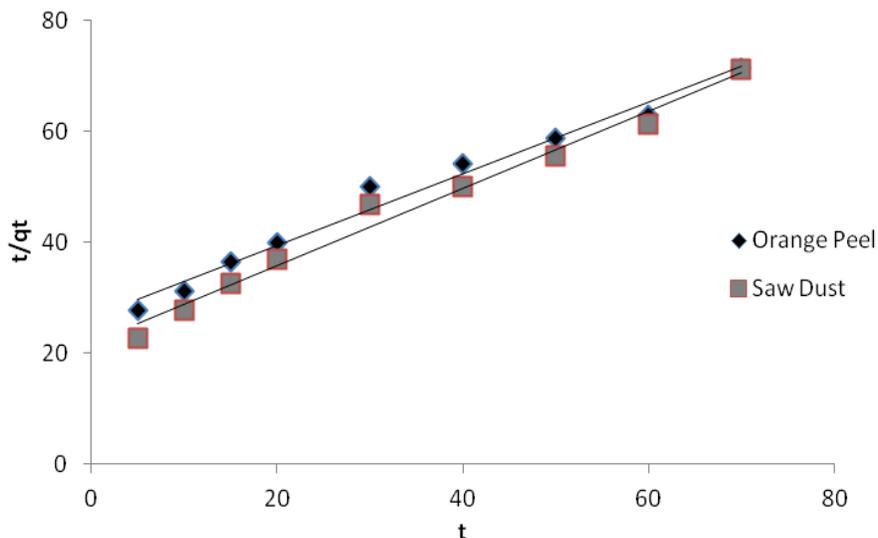


Figure 5. Pseudo-second order plot of saw-dust and Orange peel

The value of k_2 for saw dust and citrus sinensis from these plots came out to be 0.022 and 0.016 respectively, and the value of equilibrium sorption capacity, q_e , was 1.44 for saw dust and 1.55 for citrus sinensis showing that citrus sinensis has more capacity for sorption of Cu(II) as compared to saw dust.

3.6 Comparison of Citrus sinensis and Wood sawdust as biosorbents

In the present study citrus sinensis shows more Cu removal as compared to Wood sawdust.

Figures 2, 3 and 5 illustrates that citrus sinensis as a biosorbent showed slightly higher, about 1.08% more, efficiency of Cu removal, as compared to wood sawdust. Both show good bio-sorption values. This is because of high cellulose in both, lignin in sawdust and pectin component in citrus sinensis. Cellulose materials have relatively large surface areas that can provide built-in adsorptive sites to many substrates and can naturally adsorb cations in water. Citrus sinensis principally consists of cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene. These components contain various interesting functional groups such as carboxyl, hydroxyl and amido-cyanogen, which play an important role in removing the heavy metals. The FTIR results show the presence of hydroxyl functional group of carboxylic acid. The hemicelluloses contain carboxylic acid groups that are known to contribute to metal ion sorption [29].

Sawdust is principally made up of lignin and cellulose. The major components of the polymeric material in sawdust are lignin, tannins or other phenolic compounds. Proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups which are able to bind Cu^{2+} ions [53].

In citrus sinensis carboxylic groups of the pectins and the alcoholic hydroxyl groups of the celluloses as the active binding sites for metals [18]. In wood sawdust the phenolic groups of lignin and tannins are active sites for biosorption mechanism [8], [53]. So main active binding sites for copper in citrus sinensis are carboxylic groups and for sawdust, the phenolic groups are active sites.

Figure 3 shows that at pH2, pH4 and pH6.5 wood sawdust shows 3.33%, 3% and 1.08% less bio-sorption efficiency than citrus sinensis, respectively. Wood sawdust show less bio-sorption efficiency than citrus sinensis at lower pH i.e. highly acidic medium and as pH increases the efficiency gap between wood sawdust and citrus sinensis decreases. It is because of less application of phenolic sites in Cu bio-sorption as compared to carboxylic groups as metallic species show somewhat more interaction with caboxylic groups in the acidic medium [44]. Present study carried out at acidic ranges of pH i.e. less than pH7 so wood sawdust shows less biosorption than citrus sinensis. Several examples about the analysis of the relative contributions of carboxylic and phenolic groups in metal binding onto organic residue of natural biomass denotes that metallic species mainly interact with –COOH groups in the acidic range [7], [26], [38].

4. CONCLUSION

Hence, from this study, it may be concluded that citrus sinensis peel is more helpful to obtain permissible limit of divalent copper in drinking water as compared to wood sawdust and successful studies on both material could be beneficial. Copper uptake is strongly affected by pH. At higher pH deprotonation take place which results in more interaction between the negatively charged carboxylate on adsorbent and positively charged copper species. The adsorption kinetic is rapid and the equilibrium is attained after about 60 minutes of experiment. Bio-sorption increases with increase in amount of adsorbent but become almost constant after certain dose of adsorbent. Many people who live in industrial area and get drinking water from corroded copper pipes cannot afford bottled water for daily consumption. Therefore, an economically viable and easy method for bio-sorption of copper from drinking water is highly desirable. Experiments are performed on the drinking water but the study is carried out with high concentration of Cu i.e 100 ppm. This study can be applied for the removal of Cu from the waste water also and this study is fairly helpful in developing a wastewater treatment plant for the removal of Cu from the waste water by using the cheap agrowaste materials which will be economical and easy to carry out.

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