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REMOVAL OF Cu(II) IONS FROM INDUSTRIAL WASTEWATER BY CHEMICALLY MODIFIED NATURAL PLANT WASTES

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Abstract: In this study, the usability of natural wastes as low cost adsorbents for the removal of Cu (II) ions from industrial waste water has been investigated. The adsorption capacities of different natural wastes such as banana, lemon and orange peel, tea waste and sawdust of walnut were evaluated by a series of batch sorption tests. The grinded materials were classified with respect to particle size within the range of 1~2 and 0.5~1 mm. And also, the prepared adsorbents were classified as untreated, treated with acid (0.6 M of $C_2H_2O_4$) and treated with base (0.1 M of NaOH). The adsorption performances of prepared adsorbents for the sorption of Cu(II) ions were investigated by a series of batch sorption experiments. The effect of adsorbent type, modification method and adsorbent size on Cu(II) ion sorption capacities (Q_e) of the prepared adsorbents have been investigated. According to the results obtained, it has been observed that the modification with basic solution, enhanced the sorption performance of the adsorbents and exhibited the highest removal percentage up to 95% with the sorption capacity (Q_e) of 5 mg/g-adsorbent for both particle sizes of the base-modified sawdust of walnut. The equilibrium behaviour of Cu(II) sorption of base-modified sawdust of walnut was well defined by Freundlich Isotherms.

Keywords: Adsorption, natural adsorbents, copper removal

Introduction

Recently, heavy metal pollution has become one of the most serious environmental problems because of certain actions like urbanization, industrialization, and agricultural practices (*Carolina et al., 2017*). Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. The treatment of heavy metals is special concern due to their toxicological problems caused by the metals to the ecological systems and the food chain indefinitely. These metals exists a high stability and could be easily bound by living organisms which conducts to the accumulation of these components in the ecosystem *(Jeon, 2017).* Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA are summarized in Table 1 *(Barakat, 2011).* Heavy metals particularly mercury, chromium, copper, lead, cadmium, zinc and nickel have lethal effects on all forms of life even at low concentrations.

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Table 1. The MCL standards for the most hazardous heavy metals *(Barakat, 2011)*

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.010
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.050
Copper	Liver damage, Wilson disease, insomnia	0.250
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.200
Zinc	Depression, lethargy, neurological signs and increased thirst	0.800
Lead	Damage the fetal brain, diseases of the kidneys, circulatory and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys and nervous system	0.00003

Copper can be present in wastewater as the form of $CuCO_3$ or organic complexes of hydrolysis products of Cu(II) ion. Different methods can be used to remove Cu(II) ion from aqueous environment. The removal of Cu(II) ion from industrial effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods *(Pehlivan et al., 2012).* Some of these methods are as follows; chemical precipitation, membrane filtration, ion exchange, liquid extraction or electrodialysis, reverse osmosis. However, these methods are not widely used due to their high cost, low feasibility for small-scale industries and sometimes ineffective, especially when metals are present in solution at very low concentration. Recently, adsorption has become one of the alternative treatment techniques for removal of a heavy metals because of its efficiency and low cost, but conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient. Therefore, efforts have been made to use the cheapest and unconventional adsorbents such as industrial and agricaltural wastes to adsorb Cu(II) ion from aqueous solution *(Ushakumary & Madhu, 2013).* In this study, the usability of natural wastes as low cost adsorbents for the removal of Cu(II) ions from industrial waste water has been investigated. The adsorption performances of different natural wastes such as banana, lemon and orange peel, tea waste and sawdust of walnut were evaluated by a series of batch sorption tests. The grinded materials were classified with respect to particle size within the range of 1~2 and 0.5~1 mm. And also, the prepared adsorbents were classified as untreated, treated with acid (0.6 M of $C_2H_2O_4$) and treated with base (0.1 M of NaOH). The effect of adsorbent type, modification method and adsorbent size on Cu(II) ion sorption capacities (Q_e) of the prepared adsorbents have been investigated. According to the results obtained, it has been observed that the modification with basic solution increased the Cu(II) ion sorption performance of the adsorbents and exhibited the highest removal percentage up to 95% and sorption capacity (Q_e) as 5 mg/g-adsorbent for both particle sizes of the base-modified sawdust of walnut.

Methods

Materials

Orange peel, lemon peel, sawdust, banana peel and tea wastes were collected from local markets. Stock solution of Cu(II) with the concentration of 1000 mg/L was prepared $Cu(NO_3)_2.3H_2O$ and then diluted to appropriate concentrations. 0.6 M of $C_2H_2O_4$ and 0.1 M of NaOH were used for acid and base modifications, respectively. All these chemicals are supplied from Sigma Aldrich and used as analytical purity.

Preparation of Adsorbents

The collected banana peels were cut into small pieces, washed three times with tap water and three times with distilled water to remove external dirts. The wetted banana peels were kept in ambient conditions for removing the water from the surface and dried in oven at 105°C for 24 hours. The collected orange and lemon peels were dried in the sun light for 4 or 5 days. For tea wastes, soluble and coloured components were removed by washing with boiling water. This was repeated until the water was virtually colourless. The tea leaves were then washed with distilled water and were oven dried for 12 h at 85°C. Sawdusts are washed with distilled water by several times then dried at 105 °C during 1 day. The dried banana peel, orange peel, lemon peel, sawdust and tea were ground by mill and kept in bottles for further experimental uses. The grounded materials were sieved and classified as 1~2 mm and 0.5~1 mm according to particle size. Some of the adsorbents classified by particle size were kept in a remote environment from the humidity. 1 g of dried adsorbents were soaked in 20 mL of 0.6 M oxalic acid ($C_2H_2O_4$) solution for acid modification. 1 g of dried adsorbents were soaked in 20 mL of 0.1 M sodium hydroxide (NaOH) solution for base modification.

Adsorption Experiments

Batch sorption studies were achieved by contacting 0.1 g of the adsorbent with 50 mL of a solution of Cu(II) having the concentration of 10 mg/L for 24 hours at a constant temperature of 25 °C. Before and after adsorption, the concentration of Cu(II) ion have been determined with Atomic Absorption Spectrophotometer (Perkin Elmer, Varian 10+). The effect of adsorbent type, modification method and adsorbent size on Cu(II) ion sorption capacities (Q_e) of prepared adsorbents have been investigated.

Equilibrium experiments were carried out by shaking 0.1 g of the base-modified sawdust samples with 50 ml of Cu(II) solution at a concentration range 5–100 mg/L at 25 °C in a water bath for a known period of time. After equilibrium the suspension was filtered with syringe and the metal solution then was analyzed using AAS. In order to obtain the adsorption capacity, the amount of ions adsorbed per mass unit of the base-modified sawdust (mg/g) was evaluated using the following expression;

$$\boldsymbol{Q_e = \frac{(C_o - C_e)V}{m}}$$

where $\mathbf{Q_e}$ is the sorption capacity of adsorbed at equilibrium (mg/g), $\mathbf{C_o}$ is the initial metal ion concentration (mg/L), **Ce** is the equilibrium metal ions concentration (mg/L), **V** is the volume of the aqueous phase (L), and **m** is the amount of the adsorbent (g).

Equilibrium behavior of the adsorbents has been investigated by Langmuir and Freundlich Sorption Isoterm Models.

Langmuir Isotherm model is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface, which is represented by**;**

$$Q_e = \frac{q_m b C_e}{(1 + C_e b)}$$

the linear form of the equation can be written as;

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b}$$

where $\mathbf{Q_e}$ is the amount of heavy metal ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium liquid phase concentration of heavy metal ion (mg/L). $\mathbf{q_m}$ and **b** are Langmuir constants indicating adsorption capacity and energy, respectively *(Bulut & Tez, 2007).*

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term (**b**) in the Langmuir equation varies as a function of surface covarage ($\mathbf{Q_e}$) strictly due to variations in heat of adsorption *(Bulut & Tez, 2007)*. The Freundlich equation has the general form;

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

The logaritmic form of the equation is;

$$\ln Q_e = \ln K_f + (1/n) \ln C_e$$

where $\mathbf{Q_e}$ is the amount of heavy metal ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium, $\mathbf{C_e}$ is the equilibrium concentration of heavy metal ion (mg/L); $\mathbf{K_f}$ and **n** are Freundlich constant related to adsorption capacity and adsorption intensity, respectively. The plots of $\mathbf{lnQ_e}$ versus $\mathbf{lnC_e}$ were found to be linear indicating the applicability of the Freundlich model *(Bulut & Tez, 2007).*

Results and Findings

Sorption performance of modified and untreated adsorbents, regarding with removal percentages (%) and sorption capacities have been tabulated in Table 2.

Table 2. Results of removal performance of cu(ii) and sorption capacities of adsorbents

Modification	**Adsorbent**	**Particle size (mm)**	**m (g)**	**V (mL)**	**Removal (%)**	**Q_e (mg Cu/ g-adsorbent)**
1 (without NaOH)	**Orange**	1-2	0.1	50	60	3
		0.5-1	0.1		60	3
	Lemon	1-2	0.1	50	50	2.5
		0.5-1	0.1		60	3
2 (with NaOH)	**Orange**	1-2	0.1	50	30	1.5
		0.5-1	0.1		40	2
	Lemon	1-2	0.1	50	90	4.5
		0.5-1	0.1		60	3
3 (without NaOH)	**Sawdust**	1-2	0.1	50	50	2.5
		0.5-1	0.1		50	2.5
	Tea	1-2	0.1	50	60	3
		0.5-1	0.1		70	3.5
	Banana	1-2	0.1	50	30	1.5
		0.5-1	0.1		30	1.5
4 (with NaOH)	**Sawdust**	1-2	0.1	50	100	5
		0.5-1	0.1		100	5
	Tea	1-2	0.1	50	90	4.5
		0.5-1	0.1		90	4.5
	Banana	1-2	0.1	50	90	4.5
		0.5-1	0.1		90	4.5
5 (with Oxalic Asit)	**Orange**	1-2	0.1	50	0	0
		0.5-1	0.1		0	0
	Lemon	1-2	0.1	50	0	0
		0.5-1	0.1		10	0.5
	Sawdust	1-2	0.1	50	0	0
		0.5-1	0.1		10	0.5
	Tea	1-2	0.1	50	30	1.5
		0.5-1	0.1		20	1
	Banana	1-2	0.1	50	10	0.5
		0.5-1	0.1		10	0.5

Removal performances as sorption (%) of prepared adsorbents having the particle size range of 1~2 mm were presented in Figure 1.

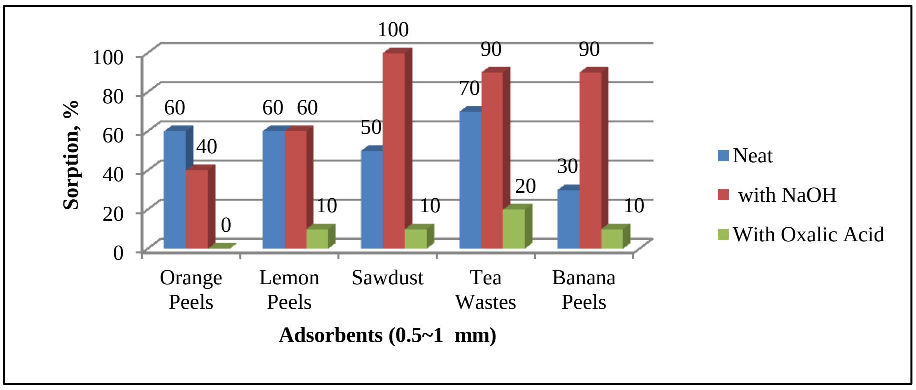


Figure 1. Removal performance of cu(ii) by 1~2 mm particle size adsorbents

As shown in Figure 1, base (NaOH) modified sawdust exhibited the highest removal performance and almost complete sorption was obtained. On the other hand acid modification inhibits the adsorbents from Cu(II) sorption. Neat adsorbents have an average removal performance of 50 – 60 %. Removal performances as sorption (%) of prepared adsorbents having the partical size range of 0.5~1 mm are presented in Figure 2.

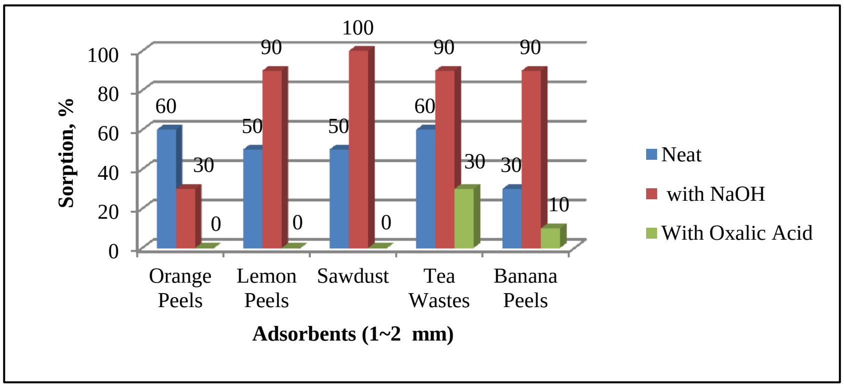


Figure 2. Removal performance of cu(ii) by 0.5~1 mm particle size adsorbents

In Figure 2, the highest removal performance of up to 95% by base-modified sawdust was obtained. It has been also observed that the acid-modified lemon peels and sawdust removal performance increased with respect to the particle size range of 1~2 mm. It was concluded that the removal performance increased as the particle size decreased. Sorption capacities of prepared natural adsorbents having the particle size range 1~2 mm and 0.5~1 mm are presented in Figure 3 and Figure 4, respectively.

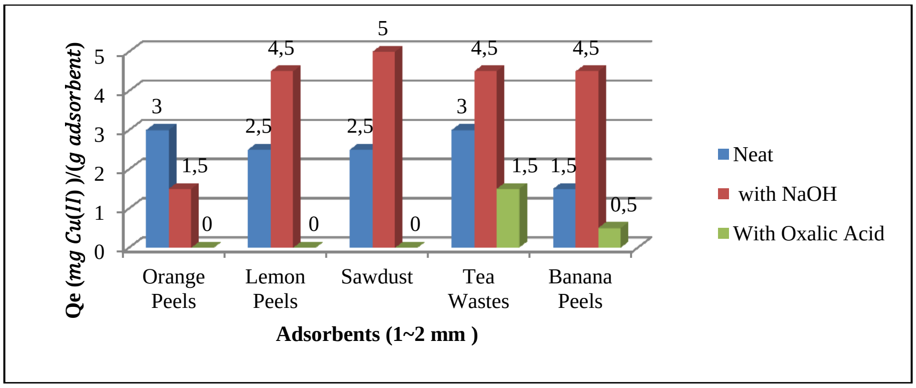


Figure 3. Sorption capacities of 1~2 mm particle size adsorbents

As shown in Figure 3, Sawdust exhibited the higest sorption capacity with the value of 5 mg Cu(II)/g adsorbent. However, the orange peels, lemon peels and tea wastes have the lowest sorption capacity. The sorption capacities of these natural adsorbents are 0 mg Cu(II) /g adsorbent.The sorption capacities of neat adsorbents are higher than adsorbents that the acid-modified. The sorption capacities of orange peels, lemon peels, sawdust, tea wastes and banana peels in 1~2 mm particle size range are 3, 2.5, 2.5, 3 and 1.5, respectively. Sorption capacities of prepared natural adsorbents having the particle size range 0.5~1 mm are presented in Figure 4.

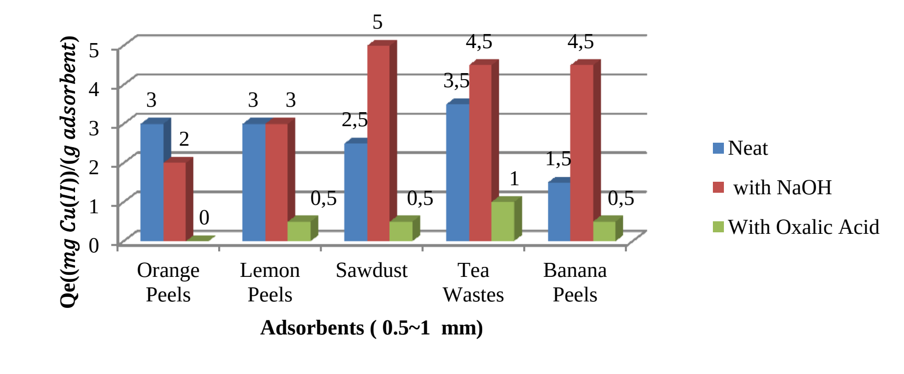


Figure 4. Sorption capacities of 0.5~1 mm particle size adsorbents

In Figure 4, sawdust modified with base exhibited the sorption capacity of (Q_e) 5 mg Cu(II)/g adsorbent. The change in particle size did not lead a major change in the sorption capacities of base-modified adsorbents and neat adsorbents. However, sorption capacities of acid-modified lemon peels and sawdust increased according to 1~2 mm particle size range. As a result of this study, the highest sorption capacity was observed in natural adsorbents modified with base, and the lowest sorption capacity was observed in natural adsorbents modified with acid. Surface area of the adsorbent is an important parameter for adsorption. Exposure of adsorbent sites for solid-metal ion interaction is high if the surface area of adsorbent is high. The smaller the particle size the higher the surface area per unit weight of adsorbent and hence higher percentage of metal removal is expected.

In this study, natural adsorbents were classified into particle sizes of 1~2 mm and 0.5~1 mm, and removal performances and sorption capacities were examined and effect of on the removal performances of neat, base-modified, acid-modified adsorbents particle size was presented on Figure 5, 6 and **7**, respectively.

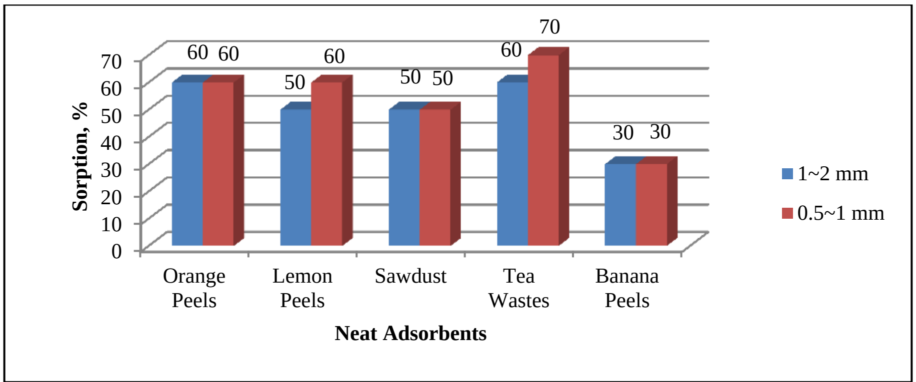


Figure 5. Effect of on the removal performances of neat adsorbents particle size

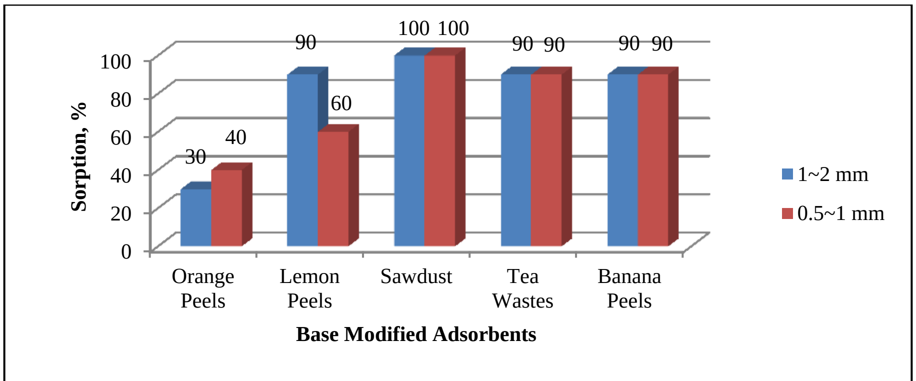


Figure 6. Effect of on the removal performances of base modified adsorbents particle size

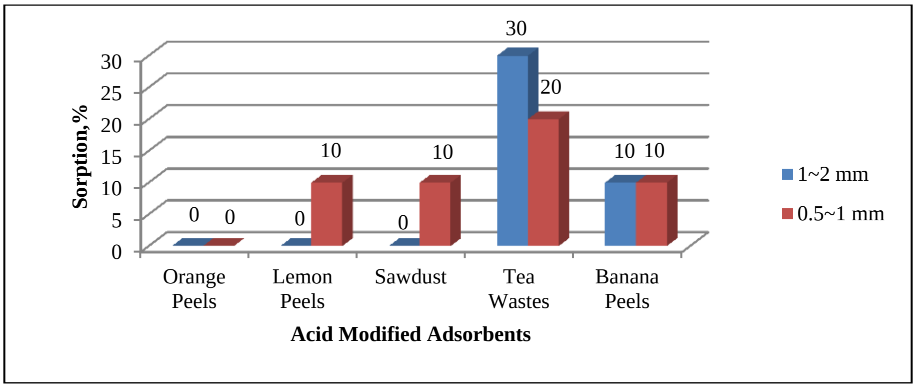


Figure 7. Effect of on the removal performances of acid modified adsorbents particle size

It can be generally concluded that the removal performance increased as the particle size decreased. Likewise, the sorption capacities of natural adsorbents have increased when the particle size decreases. Almost complete removal percentage were obtained by base-modified sawdust having the particle size of 0.5~1 mm.

Equilibrium Study

Equilibrium behaviour of based modified sawdust was presented in Figure 8.

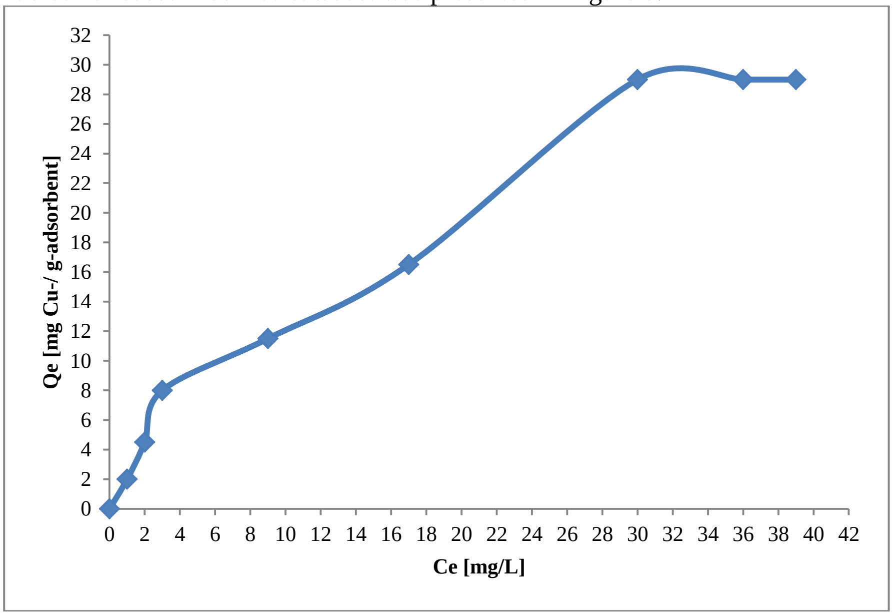
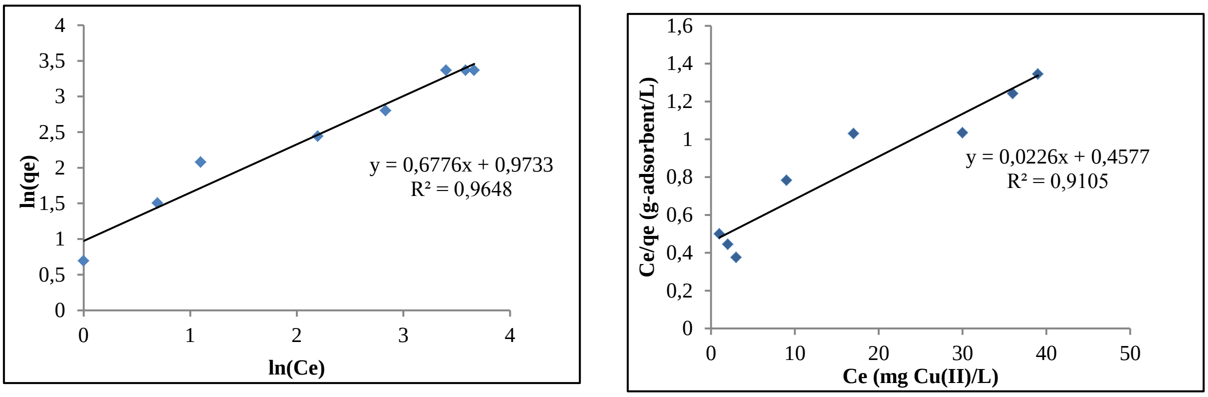


Figure 8. Equilibrium curve for the adsorption of cu(ıı) by sawdust

Freundlich and Langmuir adsorption models were used to study the interaction of Cu(II) with sawdust. The related parameters for the fitting of Freundlich and Langmuir equations are summarized in Table 3 and isotherm plots are shown in Figure 9. The Freundlich equation fitted well than the Langmuir, one as is evident from the values of regression coefficients shown in Table 3. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir type isotherm hints towards surface homogeneity of the adsorbent. This leads to the conclusion that the surface of sawdust is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon *(Ajmal et al., 1998).*

Table 3. Freundlich and langmuir parameters

Adsorbent	**Freundlich Coefficients**			**Langmuir Coefficients**		
Sawdust	**K_f**	**1/n**	**R^2**	**q_m (mg/g-adsorbent)**	**b (L/mg)**	**R^2**
	2.6467	0.6776	0.9648	44.2478	0.0494	0.9105



(a) (b)

Figure 9. Freundlich plot (a) and langmuir plot (b) for the adsorption of cu(ii) by sawdus

Conclusion

As a result of the experiments, it is observed that adsorbents treated with NaOH have higher sorption percentage and sorption capacities for Cu(II) removal than neat and acid treated adsorbents. The methyl ester groups in the orange, lemon and banana peels, tea waste and sawdust structure can be modified to carboxylate ligands by treating with a base such as sodium hydroxide, thereby increasing the metal-binding ability of the adsorbents. It is also observed that the treatment with acid reduces the sorption performance of the prepared adsorbents Because of the fact that, the protonated of the adsorption sites on the surface of the adsorbents by acid treatment. This will tend to leave the heavy metal ions in the aqueous phase rather than being adsorbed on the adsorbent surface. Cu(II) ion removal percentage of untreated sawdust is less than lemon and orange. This may be due to the lower cellulosic material contained in the sawdust. The significant effect of particle size on the sorption performance is observed for untreated tea and lemon adsorbents. According to the results of this experiment, when the particle size is decreased, the surface area is increased, and accordingly the adsorption is increased. Freundlich and Langmuir Adsorption models were used for the mathematical description of the adsorption equilibrium of Cu(II) ions to adsorbents. The sorption equilibrium data fitted well to the Freundlich isotherm model.

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