Sorption of Cu (II) Ions by Adsorption using Orange Peel

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Abstract. The purpose of the present work is to find out feasibility of the process to remove copper ions from the aqueous solution using powdered orange peel as an adsorbent. Powered activated carbon was also used along with pretreated orange peel to compare the efficiencies. Adsorption is taken into consideration to be one of the most excellent technologies broadly used in international environmental safety regions. Batch adsorption study was conducted to find out the impact related to the numerous strictures like pH, contact period, adsorbent dosage, concentration of preliminary metal Cu(II) ions besides the size of the adsorbent particle on the removal of copper ions from synthetic solutions. The statistics related to the adsorption isotherm which was obtained by carrying out the experiments, performing modeling of such data is very important so that forecasting of adsorption besides knowhow of adsorption. Experimental statistics were investigated with the use of numerous models related to the adsorption and that includes BET model, Freundlich model, Langmuir model as well as Modified Freundlich isotherms model. Equilibrium facts are also evaluated with the use of above-mentioned models related to the process of adsorption.

Keywords. Activated Carbon, adsorbent, adsorption, batch mode technique, heavy metals, adsorption isotherm, pretreated orange peel

1. Introduction

Heavy metals contamination exist in aqueous wastes due to mining operations, alloy industries, fertilizer manufacturing and garage batteries industries. To dispose off industrial effluents safely, need to give suitable treatment so as to bring contaminants within the permissible limits. The need to identify low-cost adsorbents for the cleansing of industry effluents has been a rising challenge before environmental researchers. Many of the techniques are accessible for the process regarding exclusion of numerous contaminants from wastewater, the most vital of which can be reverse osmosis, ion exchange, precipitation and adsorption. Of those techniques, adsorption is the most advocated and reliable process in evaluation to different traditional strategies (precipitation, electro-coagulation, cementing and exchange of ions on resins) due to its capability to get rid of metal ions from aqueous solutions [1, 2]. Several agricultural waste substances have been pronounced for the procedure of elimination of copper ions with usage related to the adsorption method [3]. Activated carbon is principally used as an adsorbent because of its excessive level of effectiveness, however it's usage is limited due to its higher cost. This invigorated various investigators to quest for inexpensive and locally available adsorbents so that the process can become economically feasible.

Disposing the industrial effluents containing toxic metal ions affect the flora and fauna of water bodies. Consuming water containing toxicants for drinking and cooking will harm the human health as well as animal health. There are some chemical deposits like fluoride beneath the ground in Rajasthan, Gujarat, Maharashtra, Telangana, Tamilnadu states will also caused serious health impacts on human and animal
due to prolonged consumption. Similarly, there are heavy metals like arsenic, mercury, cadmium, chromium, copper, lead, etc. also causes severe problem to the environment as well as human. The objective of the present work is for assessing the adsorption performance of Cu (II) ions onto powdered pretreated orange peel and powdered activated carbon using various adsorption isotherm models. In this paper, adsorption equilibriums were studied. Adsorption equilibrium was investigated with use of four isotherm models related to the process of adsorption like BET model, Freundlich model, Langmuir model as well as Modified Freundlich isotherms models using batch experiments.

2. Literature Review
Mohd Tahir, (2017) studied the removal process of copper, lead as well as arsenic ions using palm fibres besides orange peel individually and also in hybrid form. It was found that exothermic adsorption process in case of date palm fibres, exothermic reaction and endothermic reaction in case of hybrid action of orange peel and date palm fibre. Solid-liquid interface was found to be increased in randomness in the case of both the adsorbents, negative values were found to be for the Gibbs free energy values which are changing. Penpun Tasao (2014), conducted the research for the process of removing copper ions from the solution which was acquired using adsorption process for or pomelo peel beside depsectinated pomelo peel. There are many factors which affect the process of adsorption that include initial pH, initial metal ion concentration, contact period, temperature, etc. Author carried out research work for the parameter in terms of thermodynamics for the process of copper adsorption at the different temperatures like 25, 35 and 45 degree Celsius.
Saman Khan (2013) reported that excessive level of copper if available in the drinking water and that would have very disastrous effect not only on the human being but also for the environment. There are different treatment processes available for the removal of copper from the wastewater coming from industries as well as municipality water supply schemes and have been investigated in large extent. For the process of adsorption of copper(II), the investigator used biosorption batch studies with cheaper and locally available agro-waste like peel of citrus sinensis as well as sawdust of the wood.
Yasin Arslan, (2017) used batch adsorption method to remove chromium ions from the solution which was aqueous. Orange peel was activated with the help of potassium carbonate and that was used as adsorbent. It was found that when the orange peel activated using potassium carbonate then the adsorption capacity was higher when compared with the orange peel activated with phosphoric acid. Nthiga Wanja et al, (2015) carried out research to remove lead and copper ions as well as cadmium metal ions with the help of batch experiments to verify the efficiency of watermelon peel biomass as adsorbent. The parameter from watermelon has been modified using sulphuric acid. Various sorption parameters such as initial pH, initial metal ion concentration, dose of adsorbent as well as period required that influence the capacity of metal ions were studied.

3. Materials and Methods
3.1. Preparation of Adsorbent (Powdered-Orange-Peel)
Orange peels have been collected from the local market place. The material was washed 5-6 times using purified water systematically to remove dust as well as dirt. Washed material was sundried till it turns brittle. The dried material was crushed and made into powdered form. The powdered orange peel was dipped into the solution of 0.1 N NaOH for overnight so that content of lignin was removed and again thoroughly with double distilled water to remove alkali attached with powdered orange peel material. Alkali treated powdered orange peel material was again dipped in 0.1 N CH₃COOH for 3 to 4 hours to neutralize traces of NaOH if any attached to the material. Thereafter, the Powdered Orange Peel (POP) adsorbent material was washed with double distilled water number of times to ensure the complete removal of acid traces from the POP material. The alkali-acid washed POP material was oven dried to remove moisture content and stored in a vacuum desiccator. This pretreated orange peel material appears colourless. Powdered Activated Carbon (PAC) was acquired from nearby chemical merchant.
3.2. Preparation of Aqueous Cu\(^{2+}\) Solution
Stock solution of Cu\(^{2+}\) ions was prepared by dissolving 3.932-mg of AR grade copper sulfate salt in 1000 ml of double distilled water so as it contain 1-mg of Cu\(^{2+}\) ions in 01 ml of the stock solution (APHA, 2005). To prepare the required concentrations of Cu\(^{2+}\) ions, prepared stock solution was diluted with the required quantity of purified water. The pH of the synthetic sample was adjusted using 0.1N-HCl.

3.3. Batch Mode-Adsorption Experiments
Batch experiments were carried out so that establishment of removal of Cu\(^{2+}\) ions using pretreated powdered orange peel and PAC. In these studies, different concentrations of Cu\(^{2+}\) ions of known amount of adsorbent materials after adjusting the samples to the required pH collected into borosil glass beakers and fixed to rotary shaker and shaken at 150 rpm for a pre-quantified period. This allows all the adsorbent particles to come in contact with the Cu\(^{2+}\) metal ions.

Estimation of Cu\(^{2+}\) ions: After required period of shaking, the samples were withdrawn from the shaker and placed on a rigid platform so as to allow the adsorbent particles to settle down. The supernatant solution from each borosil flask was slowly riddled through Whatman-Strainer-Paper No.41 without disturbing the settled adsorbent particles. The filtrate was used to determine the remaining Cu\(^{2+}\) ions after adsorption using an atomic absorption spectrophotometer (AAS).

The efficiency of removal is calculated with the use following equation:

\[
\text{Adsorption (\%) } = \frac{C_o - C_e}{C_o} \times 100
\]  

(1)

\(C_o\) - the initial concentration of Cu\(^{2+}\) ions in \(\frac{mg}{l}\) and
\(C_e\) - final concentration of Cu\(^{2+}\) ions in \(\frac{mg}{l}\)
\(q_e\) - the adsorption capacity of the adsorbents (mg/g)

i.e. amount of adsorbate removed (Co-Ce) per gram of adsorbent and will be calculated as:

\[
q_e = (C_o - C_e) \times \frac{\nu}{m}
\]  

(2)

Notations are as follows,
\(\nu\) = Volume related to the used sample
\(m\) = Mass related to the used adsorbent in (g)
\(C_o\) - the preliminary concentration of Cu\(^{2+}\) ions in \(\frac{mg}{l}\) and
\(C_e\) - ending concentration of Cu\(^{2+}\) ions in \(\frac{mg}{l}\) after required period of agitation

4. Results & Discussion

4.1. Effect of pH
Initially it was aimed to study the effect of pH on process of sorption of Cu\(^{2+}\) ions in the range 2.0 to 10.0 using POP and PAC as adsorbents. After synthetic samples collected in borosil beakers and adjusted pH between 2.0 and 10.0, adsorbents (POP and PAC) were added. At higher pH (i.e. pH>6.0), the aqueous solution turned to precipitation of copper hydroxides that leads to the removal of Cu\(^{2+}\) ions and not by adsorption. Hence experiments were limited between pH 2.0 and 6.0.

Figure 1 shows that the highest adsorption of Cu\(^{2+}\) ions was noticed at 5.0 pH for both POP as well as PAC. It was detected that an upsurge in the process pH removal of Cu\(^{2+}\) ions from 42.6% to 50.2% and 55.4% to 71.4% between pH 2.0 to 5.0 with POP and PAC respectively. From the results, it was noticed that there removal of Cu\(^{2+}\) ions was higher at pH 5.0 for both POP and PAC and hence pH 5.0 considered for investigating the influence of other parameters. Similar trend was also reported by Ahsan et al 2007, Srinivas et al 2016.
At low pH the existence of H+ ions are more. As the pH increases the effect of H+ ions reduces due to the reason the surface of the adsorbent dominated with negative charge and can easily adsorb Cu2+ ions. Hence, the rate of adsorption started increasing and results in the diffusion of more Cu2+ ions.

Figure 1. Effect of pH on Biosorption of Cu2+ ions on to POP and PAC

4.2. Influence of contact period
The stock solution which contains 1000mg/l of Cu2+ ions diluted with double distilled water to 500 mg/l and pH was adjusted to 5.0. Nearly 20 flasks were used for each adsorbent (POP and PAC) to maximize contact time. In each conical flask, 50 ml of 500 mg/l Cu2+ ions were then collected and placed on the rotary shaker. To these flasks, 0.5g of POP and PAC were added separately, fixed to the rotary shaker. Immediately, rotary shaker and stop watch were started simultaneously. Rotary shaker was operated at 150 rpm. After each predefined time period (i.e. 5min, 10min, 15min, 20min, 30min, 45min, 60min, 75min, … min.), one flask at a time of each adsorbent (POP and PAC) was withdrawn from the shaker and followed the procedure mentioned in 3.3 to estimate Cu2+ ions. A graph between the percentage removal of Cu2+ ions against the contact time of POP and PAC is depicted in Figure 2. It was observed that the proportion related to the process adsorption augmented up to a certain point with an increase in contact time and after that the removal was negligible. It is also clear that in the first 30 minutes of agitation, rapid adsorption of Cu2+ ions took place due to availability of large number of active adsorption sites and then decreased the rate of uptake. As the time passes, the availability of adsorption sites decreases and hence the rate related to adsorption also decreases.
4.3. Influence of Adsorbent Dose
To investigate the influence of adsorbent dose on the removal of Cu²⁺ ions using POP and PAC as sorbents, a series of experiments were conducted with various amounts of sorbent doses. For each adsorbent, a series of 08 flasks were taken which contains 50 ml of 500 mg/l of Cu²⁺ ions concentration and then it was adjusted to pH 5.0 and fixed to the rotary shaker. To these flasks, known amounts of adsorbents (POP and PAC) such as 200, 400, 500, 800, 1000, 2000, 3000 and 4000 mg/l were added in an orderly manner and the solutions were agitated at 150 rpm for 60 min and 45 min for POP and PAC respectively. The flasks were withdrawn from the rotary shaker after required period of agitation and followed the procedure mentioned in 3.3 to find the residual Cu²⁺ ions. The results obtained are depicted in Figure 3.0.

It was evident from Figure 3 that the process of elimination of Cu²⁺ ions from the aqueous solution increased from 18.3 to 73.54 percent with POP dose increased from 0.2g/l to 4.0g/l. Further increase in dose will increase the active adsorption sites but Cu²⁺ ions available in the aqueous solution were few in number and hence the increase in percentage removal of Cu²⁺ ions was less. Similarly, the percentage removal of Cu²⁺ ions increased from 39.4% to 89.5% as the PAC dose increased from 0.2g/l to 3g/l. Based on the results obtained, considered 3.5 g/l of POP and 2.0g/l of PAC as optimum dose of sorbents for the removal of Cu²⁺ ions for further optimization of other parameters.
4.4. Influence of Initial Concentration of Cu$^{2+}$ ions

Influence of initial concentration of Cu$^{2+}$ ions has been studied at already optimized parameters in steps 4.1, 4.2 and 4.3 i.e. at pH 5.0 and contact period 60 min and 45 min, dosage of adsorbent 3.5 g/l and 2.0 g/l for POP and PAC respectively. A series of different concentrations such as 50, 100, 200, 300, 400, 500, 1000 mg/l of Cu$^{2+}$ ions were prepared using stock solution by diluting with double distilled water. All the samples were adjusted to pH 5.0 as optimized in step 4.1. 50 ml of each dilution was collected in each orderly arranged borosil flasks and added 3.5 g/l of POP and 2.0 g/l of PAC as optimized in step 4.3. These solutions were agitated at 150 rpm on a rotary shaker containing POP for 60 min and 45 min in the case of PAC as optimized in step 4.2. Samples were removed from the shaker after completion of agitation period, and followed the procedure mentioned in 3.3 to estimate the residual Cu$^{2+}$ ions.

The results obtained are depicted in Figure 4. The proportion related to the preliminary amount of moles of Cu$^{2+}$ ionsto the accessible amount of adsorption locations was found to be higher when compared with higher Cu$^{2+}$ ions concentration, and thus the lower percentage removal (Ghasemi et al 2014). Figure 4 reveals that the uptake of Cu$^{2+}$ ions has been increased from 50 mg/l to 1000 mg/l with the rise in concentration of Cu$^{2+}$ ions. In the preliminary phase, it was observed that rate of uptake was rapid (i.e. at lower concentration of Cu$^{2+}$ ions) and at later stages it was slow at higher Cu$^{2+}$ ions concentration. This was observed because the Cu$^{2+}$ ions concentration spontaneously occupied at different sites because of the availability of maximum adsorbent surface sites for adsorption.
4.5. Influence of Adsorbent Particle Size

In adsorption process, size of the particle in adsorbent plays a significant role. Since sorption is a surface phenomenon, if the particle size is smaller, the surface area is larger and therefore the removal efficiency is high. To study the effect of particle size, sieve analysis was carried out and found that the size of POP particles ranged from 1.18 mm to <0.075 mm and PAC from 150 μ to 75 μ. The results achieved are shown in Figure 5 (a) and (b).

At optimized conditions found in step 4.1, 4.2, 4.3 and 4.4, the Cu$^{2+}$ ions removal with POP was found as 46.4% & 78% with 1.18 mm & <0.075 mm size respectively. Similarly, with PAC was 70% & 91.3% with 150 micron & < 75 micron size. From Figure 5.0, it was observed that the when the dosage of adsorbent is fixed, increase in the adsorption rate with the decrease in the size of the bio-sorbent particle. This was because the greater accessibility to the pores and availability of larger surface area for bulk adsorption / unit mass of the bio-sorbent. Same tendency was also reported on the adsorption of Cu$^{2+}$ ions with the use of bagasse and fly ash as adsorbents (M.Rao, et al, 2003)

5. Adsorption Isotherms

Isotherm indicates that the amount of the adsorbate uptake on to unit weight of adsorbent to concentration of equilibrium adsorbate in the bulk fluid phase (Hema Krishna &Swamy, 2012). The analysis of adsorption data is important to develop an empirical relation based on the results obtained during experimental work. The developed equation can be used for the design purposes using the same material as an adsorbent under similar experimental conditions. To identify the best fit isotherm, four equilibrium isotherms namely Langmuir isotherm, Freundlich isotherm, BET isotherm and modified Freundlich isotherm models were chosen for process of analysis.

5.1. Langmuir Isotherm Model

The Langmuir model is based on the assumption that the maximum adsorption occur when solute molecules have a saturated monolayer on the surface of adsorbent, in such circumstances the adsorption energy remain constant and no movement of molecules of adsorbate on to the surface of adsorbent particles (Senthil Kumar, et al, 2016).
Langmuir equation is represented as follows:

\[ q_e = Q_o b C_e \frac{1}{(1+b C_e)} \]  \hspace{1cm} (3)

- \( q_e \): equilibrium adsorption capacity, mg/g
- \( C_e \): equilibrium concentration of Cu\(^{2+}\) ions, mg/l
- \( Q_o \): Langmuir constant related to the maximum amount of Cu\(^{2+}\) ions required to form a monolayer (mg/g)
- \( b \): energy of adsorption (M. Rao, et al, 2002).

The linear equation of Langmuir isotherm model is given below

\[ \frac{1}{q_e} = \frac{1}{Q_o} + \left( \frac{1}{b c_e} \right) \times \frac{1}{C_e} \]  \hspace{1cm} (4)

The values of Langmuir constants related to \( Q_o \) and \( b \) are to be attained from the linear plot of \( \frac{1}{q_e} \) on Y-axis and \( \frac{1}{C_e} \) on X-axis. The linearized Langmuir isotherms of POP and PAC are shown in Figure 6 (a, b).

\[ y = 674.55x + 0.4693 \]
\[ R^2 = 0.9945 \]  

\[ y = 213.77x + 0.2506 \]
\[ R^2 = 0.995 \]  

**Figure 6.** Isotherm of Langmuir Model for the Sorption of Cu\(^{2+}\) ions with (a) POP and (b) PAC
Langmuir isotherm has important features and can utilize for the prediction of the affinity in relation to the sorbate as well as sorbent using the separation factor ($R_L$) calculated using the following formula:

$$R_L = 1 / (1 + bC_i)$$  \hfill (5)

$b$- Langmuir constant  
$C_i$- Initial concentration of Cu$^{2+}$ ions, mg/l

The separation factor ($R_L$) using equ. 5 describes the nature of adsorption and is shown in Table 1.

| $R_L$ | Nature of Adsorption |
|-------|----------------------|
| between 0 and 1 | Favourable |
| $R_L > 1$ | Unfavourable |
| $R_L = 1$ | Linear |
| $R_L = 0$ | Irreversible |

Values of $R_L$ calculated using equ. 5 and presented in Table 3 are 0.0000014 and 0.0000023 for POP and PAC respectively lies in between 0 and 1. Hence the adsorption of Cu$^{2+}$ ions using POP and PAC is favourable and the data fitting into Langmuir adsorption model.

### 5.2 Freundlich Isotherm Model

The isotherm model given by Freundlich is an experimental relationship normally used for explaining the process of adsorption with an assumption that various adsorption sites with numerous adsorption energies.

Following is the Freundlich adsorption equation:

$$q_e = k_f C_e^{1/n}$$  \hfill (6)

The above equation can be rewritten in logarithmic form as

$$\log q_e = \log k_f + (1/n) \log C_e$$  \hfill (7)

$q_e$- amount of Cu$^{2+}$ ions adsorbed per unit mass of adsorbent, mg/g  
$C_e$- equilibrium concentration of Cu$^{2+}$ ions, mg/l  
n&$k_f$- Freundlich constants

Capacity of adsorption ($k_f$) in l/mg and $n$ gives intensity of adsorption (P. Senthil Kumar, 2010). The experimental investigations data was used to find the suitability of Freundlich model. On plotting the graph between $\log (1/C_e)$ on X-axis and $\log(q_e)$ on Y-axis and taking linear equation of all the ordinates into consideration, Freundlich adsorption isotherm constants were found from the Y-axis intercept (log $k_f$) and the slope(1/n) from the linear equation. The value of intercept i.e. log $k_f$ shall be used for the calculation of $k_f$ and the slope 1/n for ‘n’. The constants obtained a represented in Table 4. The values of $k_f$ & $n$ for POP found to be 0.0027 mg/l and 1.164 respectively and for PAC 0.0078 and 1.164. To adsorption capacity of the adsorbent is represented with the value of $k_f$. Slope (1/n) is indicating the effect of concentration on the adsorption capacity and represents the intensity of adsorption. Table 2 defines the suitability of Freundlich isotherm model (Ghasemi et al, 2014).

| “n” value | Condition |
|-----------|-----------|
| $n<1$     | Poor      |
1 < n < 2  Moderately difficult
2 < n < 10  Favourable adsorption

Figure 7. Freundlich Isotherm Model for the Sorption of Cu$^{2+}$ ions with (a) POP and (b) PAC

5.3. Brunauer–Emmett–Teller (BET) Isotherm Model
An adsorption isotherm model was developed by BET based on the hypothesis that adsorption of the molecules could be possible more than one layer thick on the adsorbent surface. Their equation is similar to Langmuir equation, that the surface of the adsorbent is mostly composed of uniform, localized as well as the process of adsorption at the locations do not interfere with the process of adsorption in the adjacent locations. Also assumed the energy related to the adsorbate is accountable for the process of adsorption of successive layers. The equation given by BET is frequently inscribed in terms of the following form (Benefield et al., 1982).
\[
q_e = \frac{(A C X_m)}{(C_s - C_e)} \times \left[ 1 + \frac{(A-1) C_e}{C_s} \right]
\]  

(8)

The BET equation has been rewritten as follows:

\[
\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{AX_m} + \frac{(A-1)}{AX_m} \times \frac{C_e}{C_s}
\]  

(9)

\(q_e\) - Solute adsorbed amount / unit weight related to adsorbent, mg/g

\(C_s\) - concentration related to the saturation in term of solute, mg/l

\(C_e\) - equilibrium condition, concentration level for the solution, mg/l

\(X_m\) - amount of adsorbate adsorbed in forming a complete mono-layer, mg/g

\(A\) = constant to describe the energy of interaction between the adsorbate and adsorbent surface

\[y = 10.173x - 0.676\]

\(R^2 = 0.8338\)
5.4. Modified Freundlich Isotherm Model

Adsorbate which is exchanged onto adsorption sites is mostly considered to be heterogeneous, which is called as mono-energetic. With the use of statistical mechanics, the following equation (10) is derived meticulously considering the assumptions that the surface of the exchanger is heterogeneous and that each class of exchange sites adsorbs independently like the Langmuir isotherm (Chitra et al., 1999)

\[ S_1 = \frac{S_{\text{max}}\infty (a_1/a_2)^\beta}{1 + \infty (a_1/a_2)^\beta} \]  

(10)

The notations are,
- \( \infty = Aa_2\beta/S_{\text{max}} \)
- \( a_1 = \) activity of solute 1 in solution
- \( a_2 = \) activity of solute 2 in solution
- \( S_{\text{max}} = \) maximum available exchange sites or cation exchange capacity
- \( S_1 = \) amount of solute 1 sorbed
- \( A, \beta = \) empirical constants.

The equation (10) modified to the Freundlich isotherm if the ratio of \( (a_1/a_2)^\beta \ll 1 \), this means that the solute which is adsorbing is in the form of trace amounts. Nevertheless, without restricting the action of the sorbing solute to trace amounts, the equation (10) is transformed to a modified form of Freundlich isotherm (equ.11) and is as follows;

\[ \log \left[ \frac{S_1}{(S_{\text{max}} - S_1)} \right] = \beta \log C_e + \log \left( \frac{A}{S_{\text{max}}} \right) \]  

(11)

In the above equations, actions have been substituted with the concentrations i.e. \( a_1 \) and \( a_2 \) in place of \( C_1 \) and \( C_2 \) correspondingly. The constant in the equation (11) \( A \) & \( \beta \) are derived using linear regression analysis. Such constant which are pragmatic and provide a means for visualizing sorption process relative to the distribution sorptive energies imported by the exchange surface.
Figure 9. Modified Freundlich Isotherm Model for the Sorption of Cu$^{2+}$ ions with (a) POP and (b) PAC

Table 3. Langmuir Adsorption Isotherm Constants

| Adsorbent | Slope, 1/Qo | Constant, 1/bQo | Regression Co-efficient, (R²) | Qo, mg/g | b | Separation Factor (R_L) = 1/(1+bC_i) |
|-----------|-------------|-----------------|-----------------------------|---------|---|----------------------------------|
| POP       | 674.5       | 0.469           | 0.994                       | 0.001482| 1438.16 | 0.0000014                      |
| PAC       | 213.7       | 0.25            | 0.995                       | 0.004679| 854.8  | 0.0000023                       |

Table 4. Freundlich Adsorption Isotherm Constants
| Adsorbent | Slope, $1/n$ | Constant, log($k_d$) | Regression Co-efficient, $R^2$ | $k_d$, mg/g | $n$ |
|-----------|--------------|------------------------|-------------------------------|-------------|-----|
| POP       | 0.859        | -2.571                 | 0.987                         | 0.0027      | 1.1641|
| PAC       | 0.859        | -2.109                 | 0.995                         | 0.0078      | 1.1641|

### Table 5. Modified Freundlich Adsorption Isotherm Constants

| Adsorbent | Slope, $\beta$ | Constant, log($A/q_{\text{max}}$) | Regression Co-efficient, $R^2$ | $\beta$ | $A/q_{\text{max}}$ | $A$ | $k_d = A/(q_{\text{max}} \beta)$ |
|-----------|----------------|-----------------------------------|-------------------------------|---------|-------------------|-----|---------------------|
| POP       | 1.813          | -3.981                            | 0.994                         | 1.813   | 0.000104          | 0.000047 | 0.00005736 |
| PAC       | 1.513          | -3.099                            | 0.991                         | 1.513   | 0.000799          | 0.000786 | 0.0000528  |

### 6. Conclusion

Equilibrium data was analysed using four different adsorption isotherms. Investigational outcomes obtained are found to be comparable with isotherm models of Langmuir model, Freundlich model and modified Freundlich isotherm model. Though the adsorption capacity of POP as compared to PAC is lower, but the cost of treatment process with POP is economical compared with costlier PAC.

### 7. References

[1] Saeed A, Akhter, Muhammed Iqbal MW 2005 Removal and recovery of heavy metals from aqueous solution using papaya wood as a new bio-sorbent Separation and Purification Technology V10 No.01 pp 25-31

[2] Habib Ahsan, NazrulIslam, AnarullaIslam And Shafiqul Alam A M 2007 Removal of Copper from Aqueous Solution Using Orange Peel, Sawdust and Bagasse . Pak. J. Anal. Environ. Chem. V08 No.01 pp 21-25

[3] Amin M T, Alazba A A and Amin M N 2017 Absorption Behaviours of Copper, Lead, and Arsenic in Aqueous Solution Using Date Palm Fibres and Orange Peel: Kinetics and Thermodynamics Polish J. of Environmental Studies V26 No.3

[4] Anastopoulos I Pashalidis I, Hosseini- Bandegheharaei, A Gianna koudakis D A, Robalds A, Usman M. Lima É. C. 2019 Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions, J. of Molecular Liquids 295 111684

[5] APHA 2005 Standard methods for the examination of water and waste water 21st edn. American Public Health Association, Washington, DC

[6] Arslan Y, Kendüzler, E Kabak, Demir B, K and Tomul F 2017 Determination of Adsorption Characteristics of Orange Peel Activated with Potassium Carbonate for Chromium (III) Removal. J. of the Turkish Chemical Society Section A: Chemistry, V4(1)pp 51-64

[7] Ben-Ali, Jaouali S, Bouissi- Najar S and Ouederni A 2017 Characterization and adsorption capacity of raw pomegranate peel bio-sorbent for copper removal. Journal of Cleaner Production,142, pp 3809-3821

[8] Benefield L D, Judkins J F and Weand B L 1982 Process Chemistry for Water and Wastewater Treatment, Prentice Hall Inc., Englewood Cliffs, New Jersey

[9] Bhatnagar A and Sillanpää M 2010 Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. Chemical engineering journal, V157 pp277-296

[10] Bhatnagar A, Sillanpää M, and Witek-Krowiak A 2015 Agricultural waste peels as versatile biomass for water purification–A review. Chemical Engineering Journal, 270, pp 244-271

[11] Chitra S, Sasidha P, Lalik B and Ahmed Jaleel 1999 The effect of common alkali and alkaline earth metal cations to the sorption of strontium and cesium onto soil. Article in Journal of Industrial Pollution Control V15. No.01pp 65-72

[12] Gupta H and Gogate P R 2016 Intensified removal of copper from waste water using activated watermelon based biosorbent in the presence of ultrasound. Ultrasonics Sonochemistry, V30, pp113-122

[13] Khan S, Farooqi A, Danish M I and Zeb A 2013 Biosorption of copper (II) from aqueous solution using citrus sinensis wood sawdust: utilization in purification of drinking and waste water. JIRRAS, V16. No.2, pp 297-306

[14] Ghasemi M, Ghasemi N, Zahedi G, Alwi, Goodarzi M and Javadian H 2014 Kinetic and equilibrium study of Ni(II) sorption from aqueous solutions onto Peganum harmala-L. Int. J. Environ. Sci. Technol. V11. pp 1835–1844

[15] Khormaei M, Nasernegad E, Edrisi M and Eslamzadeh T 2007 Copper biosorption from aqueous solutions by sour orange residue., Journal of Hazardous Materials, V149. No.02, pp 269-274

[16] RaoM, Parwate A V, Kadu P A2003Performance of low-cost adsorbents for the removal of copper and lead using low-cost adsorbent materials, J. Of Water Supply: Research and Technology – AQUA. (2003), V52 No.01, pp 49-58
[17] Rao M, Parwate A V, Bhole A G 2002 Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. Waste Management, V22, No.07 pp 821-830
[18] Mallampati R Vaityaveetil S 2013 Apple Peels A Versatile Biomass for Water Purification. ACS applied materials & interfaces, V05, No.10, pp 4443-4449
[19] Kumar Senthi P, Vincent C, Karthika K K, Kumar Satish 2010 Kinetics and Equilibrium Studies of Pb^{2+} in Removal from Aqueous Solutions by use of Nano-Silversol-Coated Activated Carbon, V27, No.02, pp 339-346
[20] Krishna R Hema, Sastry A V V S 2012 Physico-chemical key parameters, Langmuir and Freundlich isotherm and Lagergren rate constant studies on the removal of divalent nickel from the aqueous solutions onto powder of calcined brick. International Journal of Engineering Research and Development V 04, No.01, pp 29-38
[21] Shakoor M B, Niazi N K, Bibil, Shahid M, Sharif F, Bashir S S, Rinklebe J 2018 Arsenic removal by natural and chemically modified water melon rind in aqueous solutions and groundwater. Science of the Total Environment, 645, pp 1444-1455
[22] Srinivas Tadepalli, Murthy K S R, N N Rakesh 2016 Removal of Cu (II) and Fe (II) from Industrial waste water using orange peel as adsorbent in batch mode operation. International Journal of Chem Tech Research, V09, No.05, pp 290-299
[23] Tassao P 2014 Adsorption of copper using pomelo peel and depectinatedpomelo peel. Journal of Clean Energy Technologies, V02, No.02, pp 154-157
[24] Wanja N E, Murungi, Ali J, Wanjai R 2016 Efficiency of adsorption of Cu (II), Pb (II) and Cd (II) ions onto acid activated watermelon peels biomass from water. Int. J. Sci. Res, V05, No. 8 pp 671-679