COMPARATIVE STUDY OF ADSORPTION OF Cu (II) ON FRESH ORANGE PEEL AND PECTIN EXTRACTED ORANGE PEEL

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ABSTRACT

The present study was undertaken to investigate the use of waste orange peel as an adsorbent for adsorption of Cu (II) from aqueous solution after effectively extraction of value added component pectin. Four parameters affecting adsorption were studied, are pH (2.6, 4.3, 5.2, 6.8, 7.6), contact time (20, 40, 60, 80, 100 min), initial concentration (100, 200, 400, 600, 800, 1000 ppm) and adsorbent dosage (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 gm.). The optimized parameters for maximum adsorption capacity was found to be concentration of 100 ppm at pH 6 to 7, contact time 60 to 100 min and adsorbent dosage of 1 gm. for 20 ml copper solution for both adsorbents. Maximum % removal of Cu (II) for pectin extracted orange peel was found 80.95% while for fresh orange peel it is 87.30%. The kinetics study was done by fitting the equilibrium data to Langmuir, Freundlich and Tempkin adsorption isotherm. It was found that Langmuir isotherm fitted well and most appropriate to describe adsorption kinetics. The adsorption of Cu (II) for both adsorbents follows pseudo second order kinetics and rate of adsorption is controlled by film diffusion.

1. INTRODUCTION

Nowadays, use of metals in various processing industries has been increased significantly which results in production of large quantities of effluent that contains high level of toxic heavy metals causing environmental pollution. Copper is most commonly used heavy metal. Combustion of fossil fuels releases copper in air. Copper in air remains there for period of time before settling through rain and finally mix with soil. This also contaminates soil with copper. Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds settle and bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Continued inhalation of copper-containing spray cause lung cancer among exposed workers. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. Many methods, such as chemical precipitation, ion exchange, reverse osmosis and adsorption, have been used for heavy metal ions removal from various aqueous solutions. Adsorption is widely used method for this purpose as easy to carry out. Recently, adsorption process was extensively used to remove copper from aquatic medium using low cost adsorbents such as plant materials and cellulose materials, Hegazy A.E., et al.,2012.

Orange processing industries generate thousand tons of orange peel per year as a waste resulting environmental pollution. Orange peels contain many volatile oil glands in pits and galacturonic acid. Pectin is methylated ester of galacturonic acid. Pectin has its commercial value in food industries because of its gelling characteristics and the major natural additive in food products. It is utilized by food processors for conversion of fruits into products like jams, jellies, marmalades and candies. It is also used as a thickening agent for sauces, ketchup and flavored syrups and as a texturizing agent in fruit flavored milk desserts. Nowadays, pectin has also explored its value in pharmaceutical applications such as binding, thickening, suspending properties.

The adsorption of various metal ions by using agricultural waste materials has been came into light and lot of work has been done by researchers in order to establish various factors affecting adsorption. The waste is pre-treated to increase the adsorption rate. AhsanHabib, et al., in 2007 has been studied the effects of various factors such as contact time, pH, concentration, dose and ionic strength on the removal of copper ions from aqueous solution by using sawdust, orange peel and bagasse. In the year 2009, Feng Ning Chuan, et al., studied the adsorption of copper ion by modified orange peels with sodium hydroxide. Equilibrium isotherms and kinetics were obtained and the effects of solution pH value, adsorbent concentration and temperature were studied in batch experiments. Column experiments were performed to study practical applicability, and breakthrough curves were obtained. On further study by FengNing Chuan in the year 2012, Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel was done. In the year 2012, Shekhar Pandhripande, et al., have explored two methods of extraction of orange oil and pectin, namely simple distillation and leaching. The present work has been undertaken to use the waste orange peel as an adsorbent without pre-treatment. The orange peel contains commercial component pectin which is used as flavouring agent, clouding agent in various fruit industries and in pharmaceuticals. So, it has been tested that can orange peel remained after extracting pectin, be used for adsorption purpose. The comparative study of adsorption has been done between the fresh orange peel adsorbent and the pectin extracted orange peel adsorbent. For both adsorbents, any kind of pre-treatment has not been done. It has been used as it is.

2. EXPERIMENTAL

2.1. Materials And Chemicals

The fresh oranges purchased from local market of Nagpur in the month of December 2012. The peels are removed from oranges and washed two times with tap water to remove all small molecular water soluble substances. Then washed peels are dried in sunlight for one week so that peels get completely

dry and then fined ground into powder form. All chemicals used are AR graded. The stock solution of Cu (II) of 1000 ppm concentration has been prepared using copper sulphatepentahydrate. Then copper solution has been diluted to required concentration. 1 N HCl and 1 N NaOH were used for pH value adjustment.

2.2. METHOD
2.2.1. Extraction of Pectin from orange peel
50 gm of dry peels powder was simple distilled out with 150 ml distilled water. The distillation process was carried out at 80°C for two hours. After distillation, the residue in cake form was dried in atmospheric air for complete drying. Then, in 250 ml beaker, 40 gm of simple distillate dry residue powder was taken and 150 ml distilled water wad added. The pH of this prepared solution was adjusted to a value 1 by adding 1 N HCl. Elico pH meter (digital pH/ milli volt/ temperature LI615) is used to measure pH values. Then solution was heated at 70°C for extraction period of 15 minutes in a heating mantle. The heated solution was stirred manually for 5 minutes and cooled. Then the solution was filtered through Whatman filter paper. 90 ml filtrate was obtained from the solution that used for pectin precipitation. The solid residue after filtration is rinsed with deionised water and then dried. The dry powder of orange peel after pectin extraction is used as adsorbent (adsorbent 2).

2.2.2. Batchwise adsorption
The batch adsorption study was done for Cu (II) on fresh orange peels powder (adsorbent 1) and orange peels powder remained after pectin extraction (adsorbent 2). 0.1 g of adsorbent is added with 20mL of Copper ion solution of 1000 ppm in 100 mL conical flask using a shaking thermostat machine for 60 min. The effect of pH on the equilibrium adsorption of Cu(II) was investigated under similar experimental conditions between pH 2.6 to 7.8. To study effect of initial concentration of solution, concentrations varied from 100 to 1000 ppm. The effect of contact time on batch experiments was examined by varying the contact time from 20 to 100 min. Also adsorbent dosage parameter has been studied for 0.1 g to 1 g adsorbent. Then the idometric titration was performed to know the amount of Cu (II) ion in solution after adsorption.

The % removal is calculated using formula

$$\% \ Removal = \frac{Ci - Ct}{Ci} \times 100$$

Where, Ci = initial conc. of adsorbate, Ct = final conc. of adsorbate

2.2.3. Iodometric method
10 mL of the experimental copper solution after batch adsorption was taken in a 250 mL conical flask. The solution was acidified with few drops of concentrated HCl. Then requisite amount of solid sodium carbonate was added until a bluish color was observed. Then acetic acid was added, bluish color disappear. 10 mL of 10 % KI was added and kept in dark for about five minutes for iodine liberation. Due to addition of KI solution, the color changes to dark brown. After five minutes the solution was taken out. The starch solution was added in the solution. This prepared solution is then titrated with the freshly prepared sodium thiosulphate solution (0.1 M) from a burette until one changes the color to light green.

The amount of copper was calculated from the volume of thiosulfate required for titration.

3. RESULTS AND DISCUSSION
3.1. Effect of pH
The effect of pH of solution on adsorption of copper ion is shown in the figure1. The results obtained have shown that, with increase in pH of solution, the adsorption is also increasing. Approximately 55-75% adsorption was observed in acidic medium and 68-81% in basic medium of solution for orange peel without pectin extraction. For adsorbent 1, maximum adsorption found at pH 7.6 (80.95%) and less at pH 4.3 (55.55%). On the other hand, % removal for adsorbent 2 is maximum at pH 6.8 (74%) and minimum at pH 5.2 (55.55%). Also it has been observed that adsorbent 1 at 4.3 pH shows same adsorption for Cu (II) as adsorbent 2 at 5.2 pH. Thus use of adsorbent 2 for adsorption of Cu (II) only by changing pH is economical.
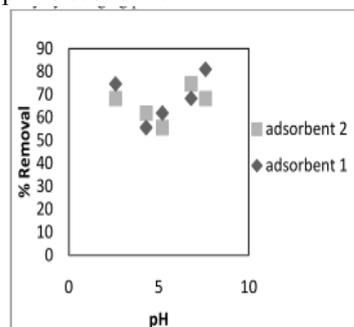

Figure 1: Effect of pH (pH= 2.6 – 7.8, adsorbent dosage= 0.1 gm, initial conc.= 1000ppm, contact time = 60 min).

3.2. Effect of contact time
Copper ion adsorption is affected by the contact time for adsorption. Figure 2shows that, the adsorption of Cu (II) is directly proportional to contact for both adsorbents. For adsorbent 1 and adsorbent 2, the adsorption is found to be maximum (74.6% and 80.95% respectively) for 100 minutes. From this, it is clear that adsorbent 2 gives better result for adsorption of copper ion in same contact time than that of adsorbent 1. The increases linearly from 20-100 min for adsorbent 2.
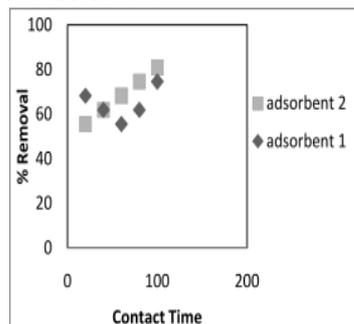

Figure 2: Effect of contact time (pH= 5.2, adsorbent dosage= 0.1 gm, initial conc.= 1000ppm, contact time = 20-100 min)

3.3. Effect of initial concentration
To investigate the effect of initial concentration of copper solution, the concentrations studied for this purpose are varied from 1000 ppm to 100 ppm. The adsorption of Cu (II) was found more for decreasing concentration of solution which is also observed to M. R. Fathi, et al., (2012). When the concentration of solution is 1000 ppm, the adsorption was found minimum i.e. 61.9%. For adsorbent 1 and for adsorbent 2 it is 55.55%. The adsorption is more i.e.

87.3% for adsorbent 1 and 80.95 for adsorbent 2 when initial concentration 100 ppm was taken. Figure 3 shows the effect of initial concentration of copper solution on adsorption of copper ion.
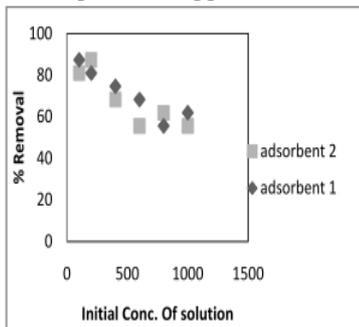

Figure 3: Effect of initial concentration of copper solution on adsorption of copper ion.
(pH= 5.2, adsorbent dosage= 0.1 gm, initial conc.= 100-1000ppm, contact time = 60 min)

3.4. Effect of adsorbent dosage

The effect of dosage of adsorbent was studied by varying values from 0.1 – 1gm. The % removal for copper ion is increased with the increase in adsorbent dosage. This was also observed in the year 2012 by M. R. Fathi, et al. Both of the adsorbent shows more adsorption for dosage of 1 gm and minimum for 0.1 gm. 87.3% adsorption was found for adsorbent 1 and 80.95% for adsorbent 2 at 1 gm. 68.25 % adsorption and 55.55 % adsorption was found at 0.1 gm of dosage for adsorbent 1 and adsorbent 2 respectively.
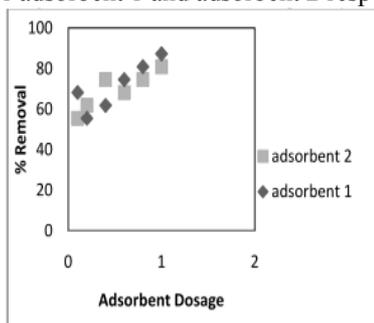

Figure 4: Effect of dosage of adsorbent on adsorption of copper ion. (pH= 5.2, adsorbent dosage= 0.1-1.0 gm, initial conc.= 1000ppm, contact time = 60 min)

4. ADSORPTION ISOTHERM

The study of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximal capacity of adsorbents. Adsorption is a function which connect the amount of adsorate to the adsorbent. The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove Cu (II), it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental sorption data. There are several isotherm models available for analyzing experimental data and for describing the equilibrium of adsorption. Generally the Langmuir equation applies to the cases of adsorption on completely homogeneous surfaces where interactions between adsorbed molecules are negligible. While the equation of Freundlich applies fairly well when describing the adsorption in aqueous systems. The correlation with the amount of adsorption and liquid phase concentration was tested with Langmuir, Freundlich and Tempkin isotherm equation.

4.1. Langmuir Isotherm

The theoretical Langmuir isotherm is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. The Langmuir equation is commonly written as:

$$\frac{Ce}{qe} = \frac{1}{qm\,b} + \frac{Ce}{qm}$$

Where, Ce (mg/L) is the equilibrium concentration of copper ion, q_e is the amount of copper ion adsorbed on orange peel at equilibrium (mg/g),q_m and b are Langmuir constants related to the capacity and energy of adsorption respectively.

The equilibrium isotherm for the adsorption of Cu (II) on adsorbent 1 and adsorbent 2 was determined with 0.1 gm adsorbent and 20 ml of copper ion solution (100-1000 mg/l) at pH 5.2. Figure 5 shows the Langmuir isotherm of adsorption of Cu (II) using both adsorbents. A plot of Ce/qe versus Ce indicate a straight line of slope $1/q_m$ and an intercept of $1/(bq_m)$. The values of qm and b were determined slop and intercepts of the plot.
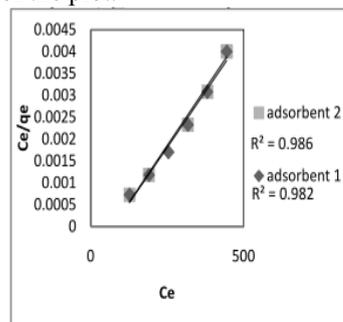

Figure 5: Langmuir isotherm plot

4.2. Freudlich Isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation can be used for non-ideal sorption that involves heterogeneous sorption. The Freundlich isotherm is commonly given by the following

$$\log q_e = logK_f + n \log Ce$$

Where K_f is a constant for the system related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of copper ion adsorbed onto adsorbent for unit equilibrium concentration. n is indicating the adsorption intensity of copper ion on to the sorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for n below 1 indicates a normal Langmuir isotherm while n above 1 is indicative of cooperative adsorption. Constants K_f and n can be calculated from slope and intercept of a plot log q_e versus log Ce.
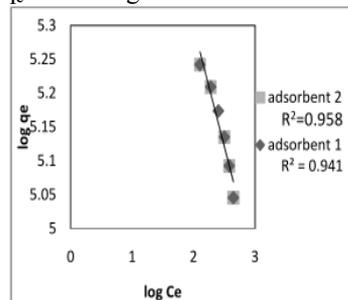

Figure 6: Freudlich isotherm plot

The adsorption isotherm for Freundlich model was examined by plotting the graph log q_e versus log Ce at pH 5.2 and dosage of adsorbent is 0.1 gm for adsorption time of 60 min.

4.3. Tempkin Isotherm

Tempkin isotherm describes the behavior of adsorption on heterogeneous surfaces. It is given by the equation below

$$q_e = a + b \log Ce$$

where, the two constants, a and b, calculated from the intercept and slope of the plot q_e versus log Ce respectively, are related to adsorption capacity and intensity of adsorption. From the isotherm model plots (Langmuir: fig.5, Freundlich: fig.6, and Tempkin: fig.7) the respective model constants are calculated and compared to know which isotherm model fits to the adsorption of Cu (II)on adsorbent 1 and adsorbent 2.
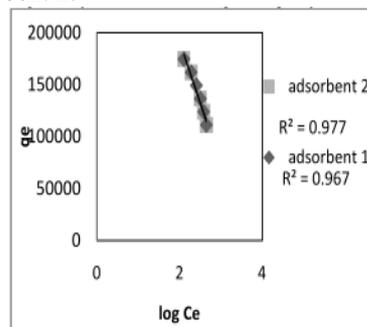

Figure 7: Tempkin isotherm plot

The values of isotherm constants are mentioned in table 1.

Table 1: Comparison of the coefficient isotherm parameters for Cu (II)

Adsorbent	Langmuir model			Freundlich model			Tempkin model		
	q_m	b	R^2	K	n	R^2	a	b	R^2
Adsorbent 1	75.82	0.2	0.982	-0.702	2.25	0.941	100000	-189703	0.967
Adsorbent 2	75.82	0.178	0.986	-0.702	2.3	0.958	100000	-189703	0.977

From isotherm constants, it became clear that the Langmuir isotherm is experimentally fitted to the adsorption of Cu (II) from aqueous solution on both adsorbents, as R^2 value of this model are 0.982 and 0.986 for adsorbent 1 and adsorbent 2 respectively.

5. ADSORPTION KINETICS

The kinetics of adsorption is required for selecting optimum operating conditions for batch process. The kinetic parameters are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption process. The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of Cu (II) on both adsorbents. The pseudo second order kinetic model was examined for the present adsorption of copper ion in aqueous solution.

5.1. Pseudo- second- order equation

The pseudo second order model equation for adsorption is given as

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

where, k_2 (mg/g. min) is the second order rate constant of adsorption, q_e is the adsorption capacity calculated by pseudo second order kinetic model. . In this kinetic model, the graph between t/q_t versus t is plotted. From this plot, values of q_e and K are determined from the slope and intercept. To be applicable the pseudo second order kinetics, the plot of t/q_t versus t should be linear.

For kinetic study, the adsorption was carried out with variation of time from 20 minutes to 100 minutes at initial concentration of aqueous solution of 1000 mg/L, pH 5.2 and adsorbent dosage of 0.1 gm. The volume of aqueous copper solution taken is 20 ml.

Adsorption capacity q_t is calculated from the formula:

$$q_t = \frac{(Ci - Ct) \times V}{m}$$

where, Ci is initial concentration (ppm) , C_t is final concentration (ppm) of aqueous solution, V is volume of solution (L) and m is the mass of adsorbent taken (mg).

From the values of pseudo second order kinetics parameters calculated from plot (figure 8), it is clear that both adsorbents are agreed to the kinetics experimentally as the value of R^2 is closer to 1.
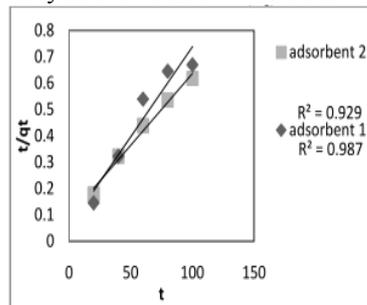

Figure 8: Pseudo second order kinetics plot for adsorption of Cu (II)

Table 2: pseudo second order kinetics model parameters for adsorption of copper ion

Sr. No.	Adsorbents	q_e (mg/L)	k_2	R^2
1	Adsorbent 1	0.005	0.054	0.987
2	Adsorbent 2	0.006	0.092	0.929

Pseudo second order kinetics is more accurate for adsorbent 1as its plot is linear than adsorbent 2.

6. ADSORPTION MECHANISM

There are four main stages in the process of adsorption:

1) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface
2) solute transport from the boundary film to the adsorbent's surface
3) solute transfer from adsorbent's surface to active intraparticular sites
4) Interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent.

One or more of these four steps controls the rate at which solute is adsorbed. The mechanism and rate controlling steps affecting the kinetics of adsorption was analyzed by Weber and Morris intra-particle diffusion model.

The Weber and Morris intra-particle diffusion model's equation is as:

$$q_t = k_p t^{1/2} + c$$

where, k_p is the intraprticle diffusion rate constant and c is the intercept of plot drawn between q_t and $t^{1/2}$. q_t is the adsorption capacity at time t.

According to this model, if the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then the intraparticle diffusion is the adsorption rate limiting step.
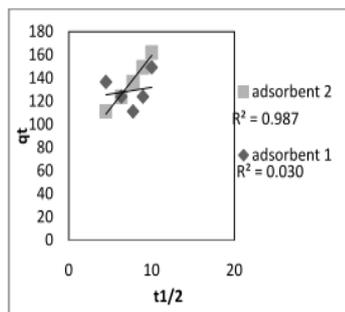

Figure 9: plot for adsorption mechanism.

From the graph (fig. 9), q_t versus $t^{1/2}$, it is clear from the values of intercept that the plots do not pass through the origin. It means that intraparticle diffusion is not the limiting step of adsorption rate. It indicates that the rate controlling step is only the film diffusion.

Table 3: comparison of rate controlling step

Sr. No.	Adsorbents	k_p	c	R^2
1	Adsorbents 1	1.16	120.1	0.03
2	Adsorbents 2	9.167	67.77	0.987

7. CONCLUSIONS

The pectin extracted peels can be used effectively for adsorption of copper ions from its aqueous solution as maximum adsorption is obtained at slightly basic pH, contact time of more than 60 min and 1 gm of peels instead of orange peels without pectin extraction. Thus, the efficient use of waste orange peel can be done by extracting pectin from it and using it further for adsorption of Cu (II) from aqueous solution, which reduces environmental problems and increases the profit of juice industries. The adsorption of copper ion on orange peels experimentally fits the Langmuir isotherm model. It follows the pseudo second order kinetics. The rate of adsorption for copper ion on orange peels is controlled by the film diffusion.

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