

CHROMIUM(VI) REMOVAL BY USING ORANGE PEEL POWDER IN BATCH ADSORPTION

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ABSTRACT

Chromium is a considerable environmental concern as it is widely used in leather tanning, electroplating, metal finishing and chromate preparation. Chromium occurs in aqueous environment in trivalent and hexavalent forms. Hexavalent chromium is more toxic than the trivalent form because of its carcinogenic and mutagenic effects. The use of adsorption provides means for cost-effective removal of Cr(VI). The natural adsorbents under consideration were orange peel powder for batch studies. The adsorbent was dried in ambient conditions for three weeks and powdered by using household grinder. The effect of important parameters such as stirrer speed, particle size, pH and concentration of adsorbate and adsorbent were studied. The orange peel powder was found to be capable for the removal of Chromium (VI) up to 98% from a synthetic Chromium solution. The change in lattice structure of adsorbent before and after adsorption was analyzed by FTIR and SEM analysis. The Freundlich and Langmuir isotherm were studied. The kinetics investigation follows pseudo second order behavior.

Keywords: Cr(VI); Natural adsorbent; Batch process ; Freundlich and Langmuir Adsorption Isotherm; Adsorption Kinetics

[I] INTRODUCTION:

Chromium is frequently present as a pollutant in the environment. However, in water, the predominant oxidation state is Chromium(VI). The two common oxidation states for Chromium in natural waters are Chromium(III) and Chromium(VI). Because of its relative insolubility under typical ground conditions, Chromium(III) is not a significant contaminant whereas Chromium(VI) from both natural and artificial sources is found in ground water. The toxicity of the Chromium depends on its chemical form. Trivalent chemical compounds are much less

toxic than those of hexavalent Chromium. Under some conditions Chromium (III) can be oxidized in soil to its toxic hexavalent form. Chromium is often present as a trace contaminant with other metals [1]. The removal of heavy metal from water and wastewater is important as most of them pose a threat to human being and environment due to their non degradability and their toxicity to the aquatic organism when discharged to receiving water. Conventional technology for removing Chromium from water and wastewater involves the precipitation,

coagulation, filtration and separation of Chromium by settling the coagulants. These conventional methods are ineffective for the removal of Cr(VI). The advanced water treatment like membrane technology is effective for the removal of Chromium(III) and Chromium(VI). Often these technologies are either expensive or leads to complex removal of Chromium from water and wastewater [2]. According to the Indian standards, the permissible limit of Cr(VI) is 0.05 and 0.1 mg/lit for potable and industrial discharge water respectively. Most of the chromites mine discharge water in process contain 2 to 5 mg/lit and the effluent from electroplating, ferrochrome and leather tanning industries contain 50 to 100 mg/lit of Cr(VI), which is much higher than the permissible limit. Cr(VI) removal or reduction in mining and industrial effluents is important before discharge into the aquatic environment [3]. There are various methods to treat Cr(VI) contaminated water such as chemical treatment, adsorption, ion exchange, solvent extraction, reverse osmosis, foam floatation, etc. [4]. Among all those processes, adsorption is an economically feasible alternate. A variety of materials have been used as adsorbent for Cr(VI) and a number of studies have been reported using adsorbents like granular activated carbon, condensed tanning gel, soya cake, activated cow dung, tyres and sawdust, activated sludge, sulphate-modified titania, activated red mud, ligno-cellular substrate, aminated polyacrylonitrile fibers, fly ash, Fe-modified steam exploded wheat straw, rice husk based activated carbon [5-8].

Keeping in view the importance of treating Cr(VI) contaminated water; the present study reports the feasibility of using a new low cost material, i.e. orange peel powder as adsorbent by batch adsorption process. The raw material is easily available as a agriculture waste.

[II] MATERIAL AND METHODS:

2.1 Material preparation and characterizations:

2.1.1 Preparation of Adsorbent

Orange which contains citric acid peels collected from fruit centre. The collected peels kept for drying for a 3 week period at room temperature. After drying

the next step was grinding and screening. Using household simple mixer grinder, the dried orange peels were grinded and converted to a fine powder. After this the orange peel powder was screened through the sieve shaker [9].



Fig: 1.0 Orange peel powder

2.1.2 Chemical:

A stock synthetic standard solution of potassium dichromate was used to prepare the adsorbate solutions of required strength. Diphenyl carbazide, H_2SO_4 , acetone, etc analytical grade chemicals were used.

2.1.3 Apparatus:

Micropipette, conical flask, magnetic stirrer, volumetric flask, whatman filter paper, funnels etc.

2.2 Adsorption:

2.2.1 Preparation of Solutions:

Diphenyl carbazide solution: Added 0.0625 gm of diphenyl carbazide in 25ml acetone and kept it in dark room.

$K_2Cr_2O_7$ solution: Added 2.84gm of $K_2Cr_2O_7$ in 1 liter of distilled water. Stirred it until homogeneous solution was obtained.

6N H_2SO_4 solution: Taken 42 ml of H_2SO_4 solution in 250 ml of distilled water.

2.2.2 Procedure:

Added 100 ml prepared $K_2Cr_2O_7$ solution in 900 ml distilled water to form one liter of solution. Taken 250 ml of the solution in a beaker and added 2 gm of adsorbent (orange peel powder) and continuously stirred the solution. Now taken 0.5 ml of adsorbent and $K_2Cr_2O_7$ solution in a sample bottle after specific time interval and added 2 ml of 6N H_2SO_4 and 2 ml of diphenyl carbazide solution. Added distilled water till the volume become 50 ml. Repeated the

procedure for the different time interval for 6 hours. Collected above samples were analyzed with the help of UV spectrometer. All the chemicals used were of analytical grade. [10-11]

[III] RESULTS AND DISCUSSION

Study was carried out for % Cr(VI) removal, adsorption capacity and adsorption kinetics & adsorption isotherm for orange peel powder as adsorbent for different parameters such as agitation speed, particle size, pH, concentration of adsorbate and adsorbent.

3.1 Effect of agitation speed:

For to study the effect of agitation speed on the adsorption of Cr(VI) from aqueous solution, agitation speed varied as 90, 120, 150, 180 and 210 rpm. Result shows that as the speed of agitation increases, adsorption increases up to certain speed. After that it remains constant with respect to change in agitation speed.

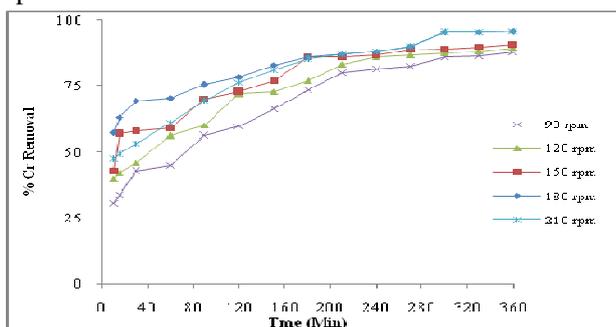


Fig: 2.0 % Cr removal for different speed of agitation with time (Condition: Chromium concentration 2 ppm, pH 1.5, adsorbent dose 2gm/250ml & particle mesh size 180)

3.2 Effect of particle size:

The adsorption efficiency increases with increase in particle mesh size.

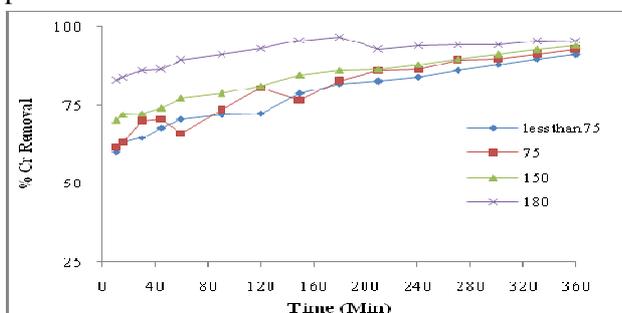


Fig: 3.0 % Cr removal with time for different particle mesh size (Condition: Chromium concentration 2 ppm, pH

1.5, adsorbent dose 2gm/250 ml and agitation speed 180 rpm).

3.3 Effect of pH:

Percentage removal of Chromium increases with decrease in pH up to 1.25. After that there was marginal rise for percentage of Cr removal for pH =1.0

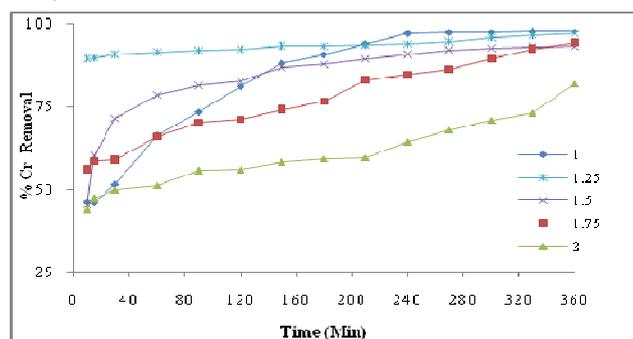


Fig: 4.0 % Cr removal for different pH on loading at different time (Conditions: Temp 30°C and adsorbent 2gm/250 ml, agitation speed 180rpm & particle mesh size 180).

3.4 Effect of adsorbent dose:

For finding out the effect of adsorbent dose for the removal of Cr(VI) from aqueous solution, adsorption study was carried out at an initial Cr(VI) concentration of 100 mg/lit with different adsorbent doses varying from 1, 2, 3, 4, and 5 gm/250ml. The results were obtained at different time intervals from 5 to 360 min. Result shown that percentage removal of Cr(VI) increases with the increase in adsorbent dosage up to 2 gm. After that marginal increase percentage Chromium removal with respect to adsorbent dose. Uptake capacity of adsorbent decreases with increase in adsorbent dose.

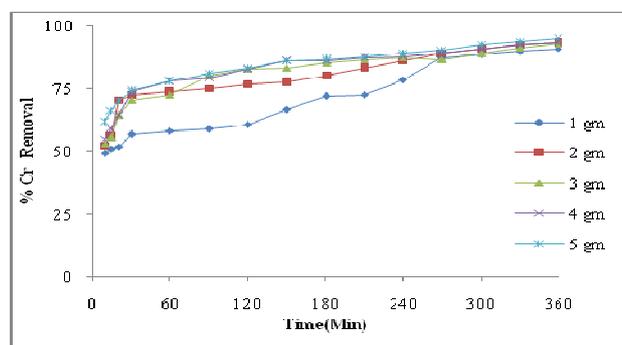


Fig: 5.0 % Cr removal with time for different adsorbent dosage (pH 1.25, agitation speed 180 rpm, particle mesh size 180)

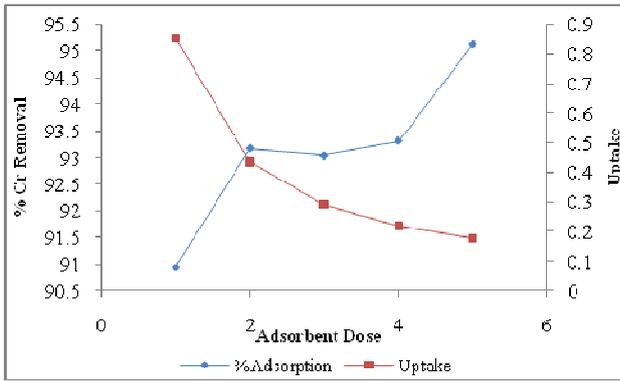


Fig.6.0 Effect of adsorbent dose (conditions: pH 1.25, temperature 30 °C, time 6 h, and Cr(VI) , concentration 2 ppm).

3.5 Effect of concentration:

The effect of concentration was studied of varying the concentration of Chromium as 1, 2, 3, 4 and 5 ppm. It was found that the % Cr removal was increases with decreases in Cr concentration

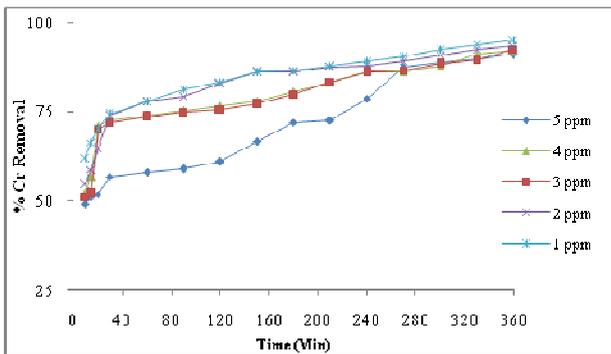


Fig: 7.0 % Cr removal with time for different adsorbate concentration (Cr conc 1 ppm, adsorbent dose 2gm/250ml, pH 1.25, agitation speed 180, particle mesh size 180)

3.6 Adsorption Isotherms:

Study and comparison of Freundlich and Langmuir adsorption isotherms for these various parameters are carried out.

3.6.1 Freundlich Adsorption Isotherm:

The Freundlich adsorption equation

$$q_e = (X/m) = K_f C_e^{(1/n)} \tag{1}$$

Where ‘q_e’ is equilibrium adsorption capacity (mg/g), ‘C_e’ is the equilibrium concentration of the adsorbate in solution, ‘K_f’, and ‘n’ are constants related to the adsorption process such as adsorption capacity and intensity respectively. The Freundlich coefficients are

determined from the plot of lnq_e Vs lnC_e on the basis of the linear form of equation given by:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{2}$$

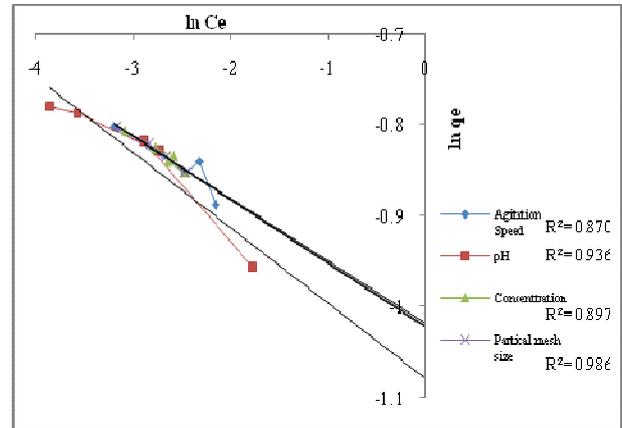


Fig.:8.0 Freundlich adsorption isotherms for variation in agitation speed, pH, concentration and particle size.

3.6.2 Langmuir Adsorption Isotherm:

The Langmuir adsorption isotherm is proposed by Langmuir, in 1918. The Langmuir equation is given as:

$$(C_e/q_e) = (1/bq_m) + (C_e/q_m) \tag{3}$$

where ‘C_e’ is the equilibrium concentration and ‘q_e’ is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent, b is adsorption equilibrium constant that is related to the apparent energy of adsorption. [12]

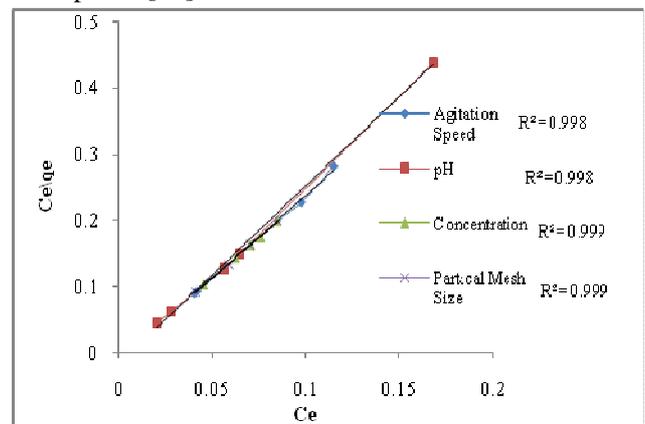


Fig:9. Langmuir isotherms for variation in agitation speed, pH, concentration and particle mesh size.

3.7 Adsorption Kinetics:

Adsorption isotherm helped in determining the properties of the adsorbents such as pore volume, pore size or energy distribution and specific surface area. The isotherm curve can also be utilized to obtain information concerning the desorption mechanism strictly connected with interaction between the adsorbent and adsorbate molecules. Therefore, the efficiency of an industrial adsorbent can be accessed through this curve. [13-14]

Freundlich and Langmuir isotherms were tested with orange peel powder. It was found that Langmuir isotherms are more closely associated.

3.7.1 Adsorption kinetic models:

The study of adsorption kinetics in wastewater is significant as it provides valuable insight into the reaction pathways and into the mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design an appropriate sorption treatment plant. It is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for adsorption. Further, it is established from the experimental observations that at optimum agitation speed, the external boundaries have hardly any effect. So application of the kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is incorrect to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous [15].

3.7.1.1 Pseudo first order kinetic model:

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid solid system was derived based on solid adsorption capacity. It is one of the most widely used sorption rate equations for sorption of a solute from a liquid solution. The overall adsorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate (qe-q). Therefore, the pseudo first order kinetic equation can be expressed as:

$$\log (q_e - q) = \log q_e - (k/2.303)t \text{ -----(4)}$$

Where ‘qe’ is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), ‘q’ is the amount of solute adsorbed at any given time ‘t’ and ‘k’ are the rate constant. ‘k’ can be calculated from the slope of the linear plot between log(qe-qt) vs ‘t’ for different adsorption parameters such as pH, adsorbate concentration, adsorbent dose, particle size and agitation speed.[16-17]

3.7.1.2 Pseudo Second Order Kinetic Model:

A pseudo second order reaction model can also be applicable to kinetics of sorption and the equation for this reaction can be shown as:

$$(dq/dt)=k(q_e/q)^2 \text{ -----(5)}$$

On integration for boundary conditions when t=0 to t>0 and q=0 to q>0 and further simplifications, above equation becomes,

$$(t/q)=(1/kq_e^2)+(t/q_e) \text{ -----(6)}$$

where h=kqe² is known as initial sorption rate where ‘k’ is rate constant .The plot of t/q Vs t at different adsorption parameters will give a linear relationship, which allows for computation of ‘qe’, ‘k’ and ‘h’.[18-19]

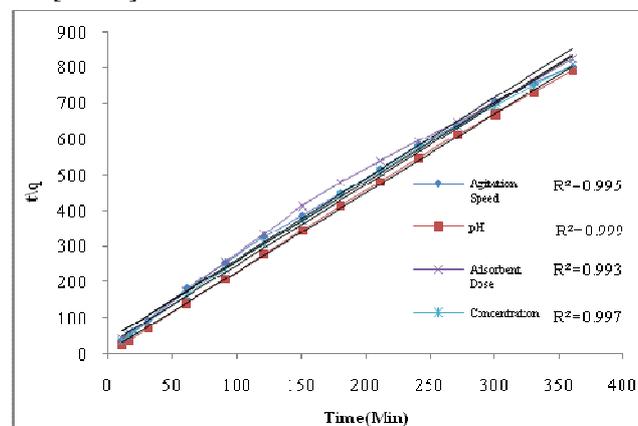


Fig: 10. Pseudo second order kinetic model for orange peel powder for agitation speed, pH, particle mesh size, adsorbent doses and concentration.

3.8 Study of rate constant:

The adsorption of Cr(VI) from liquid phase into the solid phase can be considered as a reversible process with equilibrium established between the two phases. An attempt was made to study the rate constant for adsorption of Cr(VI) on orange peel powder

adsorbent in the light of Lagergrens 1st order equation, which is, represented by

$$\log (q_e - q) = \log q_e - (k/2.303)t \quad \text{-----(7)}$$

where q_e denotes equilibrium concentration of Cr(VI) solution, q denotes the residual Cr(VI) concentration, K the specific reaction rate for adsorption process, t denotes time (min) and the plot $\log(q_e - q)$ versus t at fixed adsorbent (2gm/250 ml) doses. The result was a linear relationship. Investigation was carried out at ambient temperature. Pseudo second order kinetics model [20] was applicable to this sorption process and the simplified equation for this reaction was

$$(t/q)=(1/kq_e^2)+(t/q_e)=(1/h)+(t/q_e) \quad \text{-----(8)}$$

where k is the rate constant. t/q versus t values are plotted. The correlation coefficient (R^2) and rate constant (k) is found. From the values of R^2 it is concluded that the sorption process followed pseudo second order kinetics.

[IV] ANALYSIS OF ADSORBENT:

4.1 SEM (Scanning Electron Microscope) images

1) **Orange peels before adsorption :**

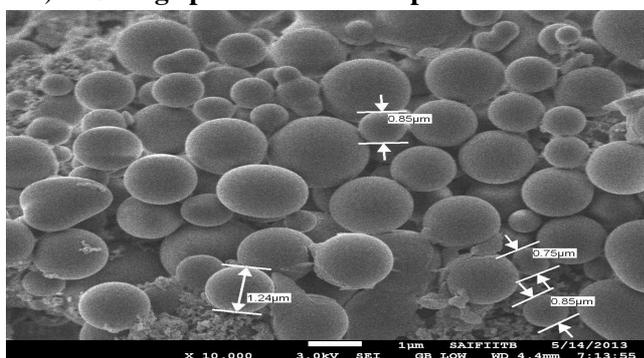


Fig: 11. SEM Image for orange peels before adsorption

2) **Orange peels after adsorption :**

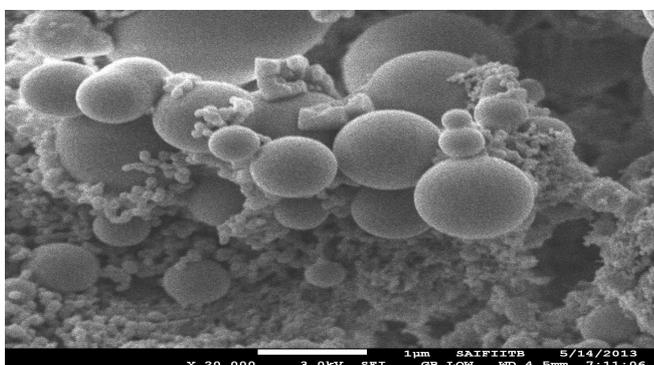


Fig: 12. SEM Image for orange peels after adsorption

4.2 BET (Brunauer – Emmett – Teller) Method:

Brunauer–Emmett–Teller (BET) theory serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The BET method is widely used in surface science for the calculation of surface areas [17-18].

Test	Observation	Conditions
Surface Area	0.84 m ² /gm	Temperature : 110 ⁰ C Purge Gas : Nitrogen Time Duration : 30 min

4.3 FTIR (Fourier Transform Infrared Spectrometry)

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer [21].

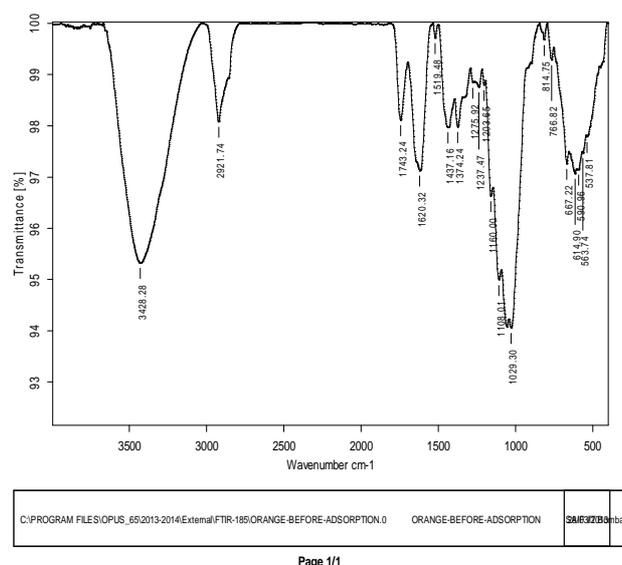


Fig: 13. FTIR image for orange peel powder before adsorption

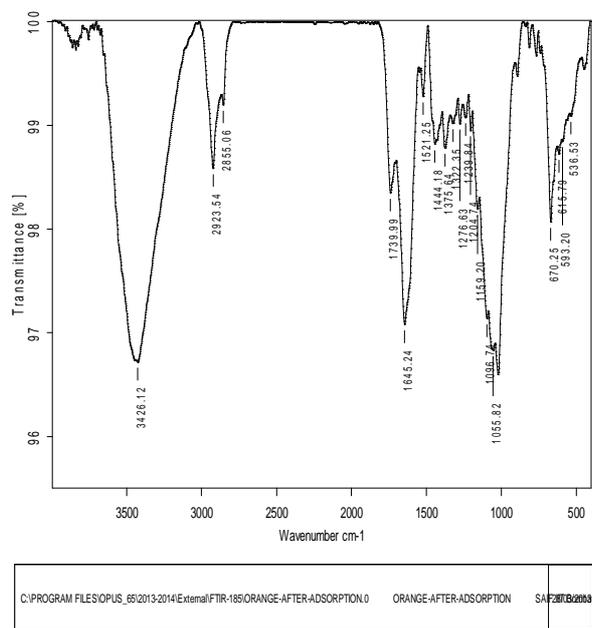


Fig. 14. FTIR image for orange peel powder after adsorption

CONCLUSION

Orange peel powder adsorbent has been found to be effective for removal of Cr(VI) from aqueous solutions. The adsorption process followed a pseudo second order kinetics and obeyed the Freundlich and Langmuir isotherms. Low concentration Cr(VI) in solution promoted its efficient removal from the solution and it increased with increase in the adsorbent doses. Due to easy availability and high efficiency of orange peel powder, it can be effectively used for removal of Cr(VI) from solution.

The study was carried out by varying time, agitation speed, pH, particle size, concentration of adsorbate and adsorbent. Effect of agitation speed shown that adsorption increases with increase in agitation speed up to 180 rpm and after that it remains constant (Fig. 2.0). It was also observed that (Fig. 3.0) adsorption efficiency increases with increase in particle mesh size. It was evident (Fig. 4.0) that the percentage adsorption was higher at lower pH. Uptake capacity of adsorbent decreased with increase in adsorbent dose (Fig. 6.0). It was observed that the percentage of

adsorption decreased with the increase of adsorbate concentration (Fig. 7.0). The efficiency of adsorption changed for various parameters. The increase in adsorption efficiency may be due to the change in the lattice structure of adsorbent. This was amply proved from various physical structure analyses like SEM and FTIR, which showed different phases with higher number of holes or sites available for adsorption (Fig.11-14).

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