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Adsorption Of Phenol From Aqueous Solution By Allium Sativum Linn Peel

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ABSTRACT

The adsorption studies of phenol from aqueous solution on allium sativum peel have been studied in the range of 50-250 mg/L initial phenol concentration .The study was carried out as function of contact time, pH, initial phenol concentration,allium sativum Linn peel dosage and temperature. The experiment demonstrated the maximum phenol was obtained at in pH of 2 and it takes 6h to attain equilibrium .The adsorption data was analyzed using the Langmuir and Freundlich isotherm models and it was found that Langmuir isotherm model represented the measured sorption data well. Batch adsorption models based on the assumption of the pseudo-first order and pseudo-second order mechanism were applied to examine the kinetics of the adsorption. The results showed that kinetic data were followed more closely the pseudo-second order model than the pseudo-first order

Keywords: Adsorption,diffusion,equilibrium isotherm, kinetics phenol.

1. Introduction

Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. It is a derivative of benzene, is an important raw material and/or product of chemical and allied industries (e.g. petrochemicals, oil refineries, plastics, leather, paint, pharmaceutical, steel industries and pesticides). It is highly soluble in water and is very toxic in nature. It is a colorless, hygroscopic and crystalline substance, which turns pink in air owing to its oxidation. It is a weak acid dissociating slightly in aqueous solution. For this reason it is also known as carbolic acid. The Ministry of Environment and Forests (MOEF), Government of India and EPA, USA, have listed phenol and phenolic compounds on the priority-pollutants list. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances. The MOEF has set a maximum concentration level of 1.0 mg/l of phenol in the industrial effluents for safe discharge into surface waters, the WHO recommends the permissible phenolic concentration of 0.001 mg/l in potable waters. That phenol is highly toxic and difficult to degrade biologically have led to setting up of rigid limits on the acceptable level of phenol in the environment. Phenol is also toxic to plants and aquatic life, which is reflected by low acceptance criteria where these receptors are to be protected. Different water treatment technologies are used to remove phenolic pollutants. Destructive process such as destructive oxidation with ozone, hydrogen peroxide, or manganese oxides and recuperative process such as adsorption into porous solids (Tor et.al.,,2006),membrane separation and solvent extraction. Adsorption is a well-known removal technique for organic compounds from water, but the cost of adsorptive removal process is high when pure sorbents (i.e. activated carbon, etc.) are used due to their high price. Consequently, the cost of pure adsorbents may be a limitation for many treatment applications and there is a strong motivation to find cost-efficient alternative sorbents obtained from industrial and agricultural waste such as bagasse fly ash **(**Rong et al.,2005) petroleum coke[3], paper mill sludge, red mud , fertilizer and steel industries waste[4], lignin ,wood charcoal[5], etc.

This study was to investigate the adsorption potential of Allium sativum linn peel for the removal of phenol from aqueous solutions. The structure of Allium sativum linn peel is characterized by Fourier Transform Infrared (FTIR) spectroscopy. The effects of experimental parameters such as initial pH of the solution, contact time, initial phenol, concentration, adsorbent dosage, temperature were studied. The adsorption mechanism of phenol onto Allium sativum were evaluated in terms of kinetics. The adsorption isotherms were described by using Langmuir and Freundlich isotherm models.

2 .Materials and Methods

2.1Adsorbent and their Characterization

Allium sativum linn peel collected from local market was washed with distilled water to remove the water soluble adherent impurities. This was followed by drying in to get rid of the moisture and other volatile impurities. The dried peel were grounded and sieved to a uniform particle size.The FTIR Spectra in the wave numbers ranging from 3500 to 500 cm^{-1} of the Allium sativum linn peel are presented in Fig 2.1 The characteristic bands at 3543 - 3528 cm^{-1} as a broad bands is assigned to OH stretching vibrations(V_{oH}) which may arise from the isomorphic substitution in the tetra and octahedral

layers. The characteristic bands at 505 -544 cm^{-1} as a broad bands is assigned to amino groups.

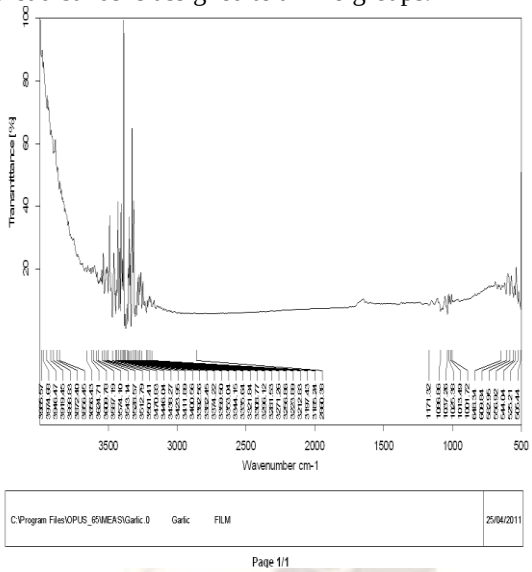

Fig 2.1 FTIR spectra of Allium sativum linn peel

2.2 Adsorbate

Phenol of analytical reagent grade (AR) supplied by southern scientific corporation India chemicals Ltd., India. It was used for the preparation of the synthetic adsorbate solution of various C_o in the range of 50-250 mg/l. stock solution as required was prepared every day and was stored in a brown color glass reservoir of 2 litre capacity to prevent photo oxidation. The C_o was as certained before the start of each experimental reaction.

2.3 Analysis of phenol

The concentration of phenol in the aqueous solution was determined using a UV spectrophotometer at wavelength 510nm.Prior of analysis, a technical calibration curve has been obtained and it was very reproducible and linear over the concentration range used in this work, no disturbance of supernatant of the Allium sativum linn peel exhibited at this particular wavelength.

2.4 Adsorption studies

For each experiment, 100 ml of the phenol stock solution of known C_o,pH_o and a known amount of adsorbents were taken in a 250 ml of stoppers conical flask. This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 120 rpm. Small amount of the sample was withdrawn after 30 min and was filtered through whatman filter paper no.42 and analyzed for phenol concentration.The percentage removal of phenol and equilibrium adsorption uptake were calculated.

3. Results And Discussion

3.1 Effect of initial concentration

The effect of C_o on the extent of adsorption on allium sativum linn peel as a function of time is shown in Fig 3.1. At any time the amount of phenol adsorbed per unit weight of adsorbent increased with increasing C_o. The C_o provides the necessary driving force to overcome the resistances to the mass transfer of phenol between the aqueous and the solid phases. The increase in C_o also enhances the interaction between phenol and the allium sativum linn peel . Therefore, an increase in C_o of phenol enhances the adsorption uptake of phenol.[6]

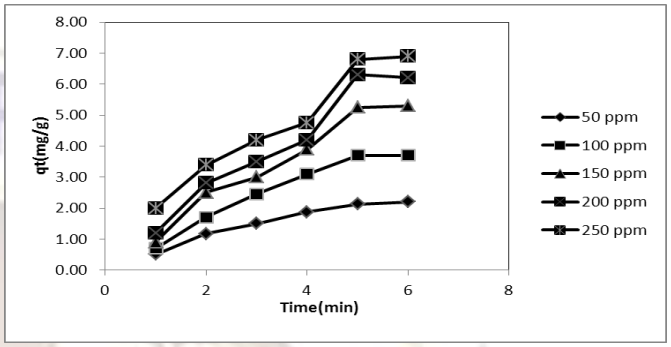

Fig 3.1 Effect of initial phenol concentrations
(pH: 7.5, *T*: 30◦C, *t* : 6 h, dosage: 2g, speed : 120rpm)

3.2 Effect of pH

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. Fig.3.2 shows that, the uptake of phenol increased with decreasing initial pH and was the greatest at pH 2.0. The pH primarily affects the degree of ionization of the phenol and the surface properties of allium sativum linn peel. At low pH values, the functional groups of allium sativum linn peel would be protonated and result in a stronger attraction for negatively charged ions in the adsorption medium. Phenol being weakly acidic would be partially ionized in solution. These ions will be negatively charged and will be directly attracted due to electrostatic forces by the protonated amino groups of the allium sativum linn peel. As the pH increased, the overall surface charge of the allium sativum linn peel became negative and adsorption decreased.[7]

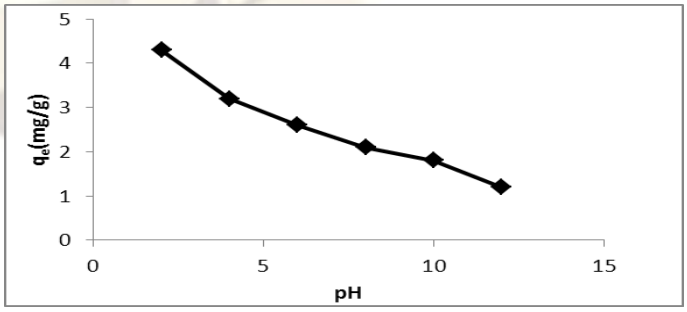

Fig 3.2 Effect of pH on the phenol adsorption
(C_0 = 50mg/l, pH: 7.5, *T*: 30◦C, *t* : 6 h dosage: 2g, speed : 120rpm)

3.3Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter because this parameter determines the capacity of adsorbent for a given phenol concentration and also

determines sorbent–sorbate equilibrium of the system. The effect of adsorbent dosage on the adsorption of phenol was determined within the adsorbent dosage range of 0.5–2.5 g and the results are represented in Fig. 3.3 It is known that the increase in adsorbent concentration resulted in decreased the adsorption amount due to the partial aggregation or overlapping of adsorbent, which results in a decrease in effective surface area for the adsorption. Therefore, the optimum amounts of allium sativum linn peel adsorption experiments were selected as 1.5g[8]

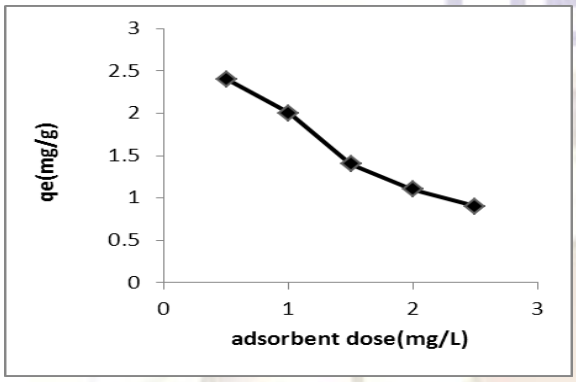

Fig 3.3: Effect of adsorbent dosage
(C_0 = 50mg/l, pH: 2, T: 30◦C, t : 6 h, speed : 120rpm)

3.4 Effect of temperature

The effect of temperature on the removal efficiency was investigated in the temperature range of 25–45 ◦C. The experiments were carried out with allium sativum linn peel of 1.5 g and initial phenol concentration of 50mg/l pH 2. when increasing the temperature from 25 to 45 ◦C, indicating that phenol uptake was favored at lower temperatures Fig.3.4. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species Similar results were obtained by literature. with adsorption of 2,4,6-trichlorophenol by activated clay.[13]

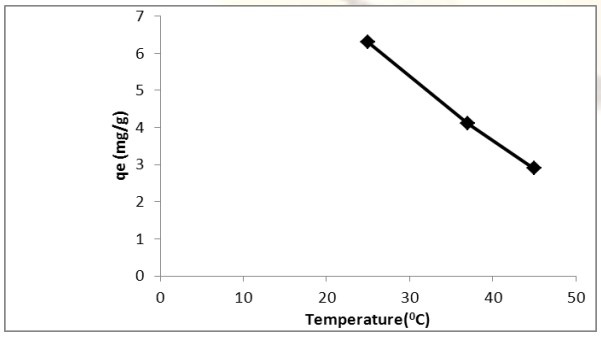

Fig 3.4 Effect of temperature
(C_0 = 50mg/l, pH: 2, t : 6 h, dosage:1.5g, speed : 120rpm)

4. Kinetic model

Adsorption kinetic is important from the point of view to control the process efficiency. Various kinetic models have been used by various researchers, where the pseudo-first-order and pseudo-second-order models were studied. The mechanism of adsorption depends on the physical and/or chemical characterstics of the adsorbent as well as on the mass transfer process. The kinetics of adsorption is important from the point of view that it controls the process efficiency. Various researchers has been several kinetics models,where the adsorption is treated as a pseudo first order and pseudo second order process.In the present study the adsorption of phenol by allium sativum linn peel has been described by the pseudo second order model.The pseudo-first-order rate equation of Lagergren is generally described by the following equation:

$$\frac{dq_t}{dt} = K_t(q_e - q_t)$$

Where k_t is the pseudo-first-order rate constant. After integration,by applying the conditions, q_t=0 at t=0 and at t=t, q_t=q_t, the above Equation becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_t}{2303(t)}$$

Where q_e is the amount of phenol adsorbed at equilibrium in mg/g. Value of k_t was calculated from the plots of log (q_e−q_t) versus t for different concentrations of phenol.

The pseudo-second -order kinetic model is expressed as follows:

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

Where k_2 is the second-order rate constant (g/mg min), by plotting of t/q versus t is a linear relationship. Values of $k_2$and q_e . were calculated from the intercept and slope of the plots of t/q versus t. The results of k_2 and correlation coefficients (r^2) were shown in Table.1.The correlation coefficients of the second-order kinetic model were greater than the first-order kinetic model.[11]

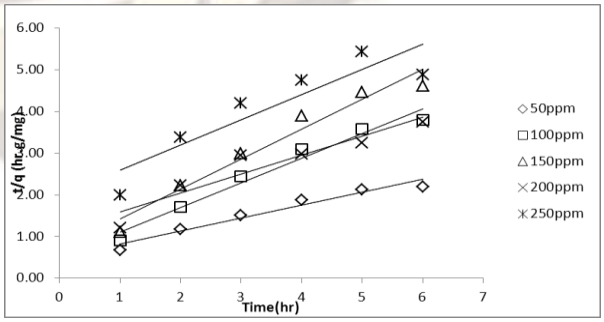

Fig 4.1:pseudo First order plot for adsorption of phenol
(C_0 = 50mg/l, pH: 7.5, t : 6 h, dosage:2g , speed : 120rpm)

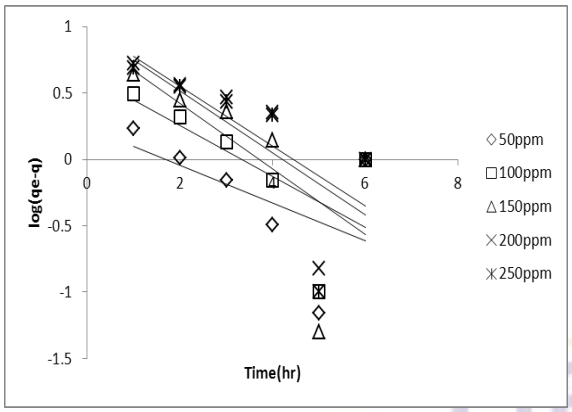

Fig 4.2: pseudo second order plot for adsorption of phenol
(C_0 = 50mg/l, pH: 7.5, t : 6 h, dosage:2g , speed : 120rpm)

Table :1 kinetic constants for phenol-Allium sativum Linn peel adsorption

Con. (mg/l)	$q_{e,exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		$K_1(h^{-1})$	$q_{e,cal}$ (mg/g)	R^2	$K_2(h^{-1})$	$q_{e,cal}$ (mg/g)	R^2
50	2.20	0.142	1.725	0.284	0.192	3.2	0.969
100	3.7	0.191	4.315	0.446	0.679	3.0	0.954
150	5.3	0.247	8.260	0.440	0.733	5.7	0.956
200	6.2	0.225	10.02	0.559	0.180	5.8	0.895
250	6.9	0.234	9.66	0.503	0.182	6.2	0.821

5. Adsorption Isotherms

Adsorption isotherm reflects the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. It provides essential physiochemical data for assessing the applicability of the adsorption process as a complete unit operation. Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process [9,10]. The model parameters can be construed further, providing understandings on sorption mechanism, surface properties, and an affinity of the adsorbent.The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature[12]. Contrarily to Langmuir, Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy level. The Freundlich describes reversible adsorption and is not restricted to the formation of monolayer.The linear form of Langmuir and Freundlich equations are represented by equation(3) and (4) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \text{ ----------(3)}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{ -----(4)}$$

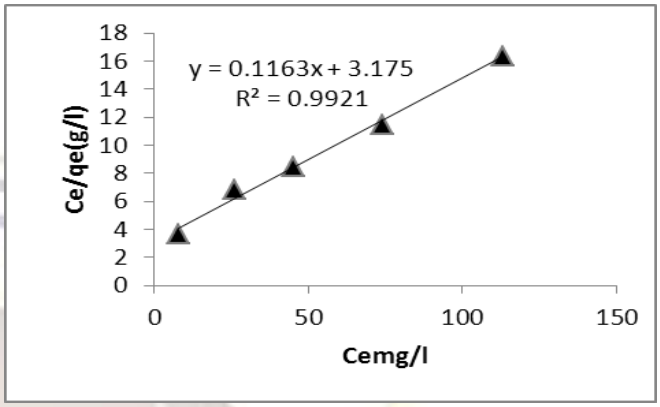

Fig 5..1 Langmuir isotherm plot
(T:30°C,t:6h,dosage:2gm/l, C_o:50mg/l,pH:7.5)

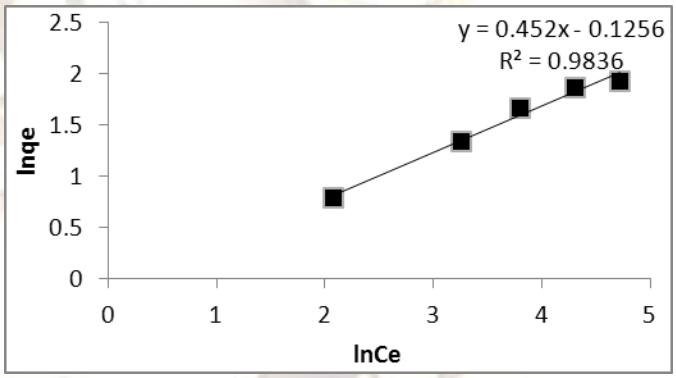

Fig.5.2:Freundlich isotherm
(T:30°C,t:6h,dosage:2gm/l, C_o=50mg/l pH:7.5)

Table2. Langmuir and freundlich coefficients

Adsorb.	Langmuir parameters				Freundlich parameters		
	Q_o (mg g^{-1})	K_L (lg^{-1})	a_L (l mg^{-1})	R^2	K_f (mg g^{-1})(lm)	n	R^2
Alliu m sativ um linn	8.62	0.315	0.036	0.992	0.88	2.21	0.983

6. Conclusion

In this study, the adsorption of phenol from aqueous solution was investigated using a Allium sativum Linn peel.The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial phenol concentration. The optimum pH value was found to be 2.0. The Langmuir and Freundlich adsorption equations were used to express the adsorption phenomenon of the phenol.The

equilibrium data were well described by the Langmuir model.The pseudo-first order and pseudo-second order kinetic models were used to analyse data obtained for phenol adsorption onto Allium sativum linn peel. The results indicated that the pseudo-second order equation provided the better correlation for the adsorption data. It can be concluded that the Allium sativum Linn peel is an efficient adsorbent for the removal of phenol from aqueous solution.

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