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REMOVAL OF PHENOL FROM WASTE WATER USING MANGO PEEL

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***Abstract*— Phenolic compounds are found in wastewaters of various industries such as petroleum refining, coal conversion, plastics, textiles, iron and steel manufacturing as well as pulp and paper manufacturing. It is very important to remove phenols and aromatic compounds from contaminated water before discharge into any natural water because of their toxicity to aquatic organisms. Conventional processes for removal of phenols from industrial wastewaters including extraction, adsorption on activated carbon, bacterial and chemical oxidation, electrochemical techniques, irradiation, etc. suffer from serious shortcomings such as high costs, incompleteness of purification, formation of hazardous by-products, low efficiency and applicability to a limited concentration range (these methods are not suitable for treating moderate to high concentrations of phenols). In this project, we have used mango peel as an adsorbent to treat the synthetically prepared phenol solution. The effectiveness of the adsorbent is measured by finding out the concentration of phenol in the treated solution by the use of ultraviolet spectroscopy. The mango peel adsorbent was activated using three different activating agents and the following parameters of adsorption have been studied: effect of contact time, effect of pH, effect of temperature, and effect of adsorbent dosage.**

***Index Terms*— Activated carbon, agricultural waste, mango peel, phenol removal, wastewater treatment**

I. INTRODUCTION

A number of effects from breathing phenol in air have been reported in humans. Short-term effects reported include respiratory irritation, headaches, and burning eyes. Chronic effects of high exposures include weakness, muscle pain, anorexia, weight loss, and fatigue. Effects of long-term low-level exposures include increases in respiratory cancer, heart disease, and effects on the immune system [1].

Repeated exposure to low levels of phenol in drinking water has been associated with diarrhoea and mouth sores in humans. Ingestion of very high concentrations of phenol has resulted in death. In animals, drinking water with extremely high concentrations of phenol has caused muscle tremors and loss of coordination [2].

At lower concentrations of phenol, techniques like solvent extraction, incineration, chemical oxidation, biological degradation, adsorption, and membrane separation cannot be used to treat the wastewater. Additionally, these become uneconomical for their industrial scale-up operation.

The methodology used in this project is unique in its sense because it includes a study of various parameters that affect the adsorption efficiency of the user defined adsorbent, and an effort is made to make the process as economical as possible by preparing the adsorbent using agricultural waste.

II. METHODOLOGY

A. *Preparation Of Adsorbent*

The mango peel was first washed with tap water to remove impurities and then with distilled water, and kept under the sun to dry for a period of almost 1 week. The adsorbent was then carbonized by heating it upto a temperature of around 200 ° C in the absence of oxygen. We then used a ball mill to crush the adsorbent to reduce its size into smaller particles. The adsorbent was then sieved and activated by the procedure shown below.

B. *Activation Of Adsorbent*

20gms of adsorbent was taken in three different beakers. To these; 20ml of concentrated hydrochloric acid, 20ml of concentrated sulphuric acid, and 20ml of orthophosphoric acid were added respectively, and kept for 48 hours with regular stirring every hour. The beakers were then heated for 6 hours at a temperature of about 160℃. The contents of the beakers were washed with tap water to remove impurities, decanted and washed again and decanted again. The process was repeated 2-3 times until a pH of around 7 was maintained. The adsorbent was then filtered and dried.

C. *Preparation Of Phenol Solution*

A 1000ppm phenol solution was made by adding 0.94ml of 100% phenol in a 1 litre standard flask and made up to the mark with distilled water. From this, 20ppm, 40ppm, 60ppm, 80ppm, and 100 ppm solutions were made by pipetting out 2ml, 4ml, 6ml, 8ml, and 10ml of the base solution, respectively, into 100ml standard flasks.

D. *Calibration Of Solution*

The equipment used for the measurement of phenol concentration was an Ultraviolet-Visible Spectrometer. To establish a reference for measurements, a base line correction was carried out by filling both the cuvettes with the blank solution and using the option of base line correction on the

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spectrometer. The phenol solution was then placed into the sample cuvette to get a graph of the ultraviolet absorption of the solution over the range 0nm to 600nm. The value at the peaks which gives the wavelength of absorption for the given concentration of phenol was found out. The process was repeated for all concentrations of phenol and a graph of absorbance vs. concentration of phenol was plotted. The results are shown in Table 1 and Fig.1.

E. *Effects Of Varying Parameters On Adsorption*

Following are the methods for determining how various parameters affect adsorption:

1. Effect of contact time

Three conical flasks, having 100ml of 20ppm phenol solutions each, were taken and 0.25gm of the activated adsorbents added respectively. The setup was placed in a shaker. The amount of phenol left in the solution was measured using ultraviolet spectroscopy every 30min for one hour followed by every hour for 5 hours until the solution reached equilibrium. A graph of concentration vs. percentage of phenol removed was plotted. The process was repeated for 40ppm, 60ppm, 80ppm and 100ppm solutions.

2. Effect of pH

Five flasks having 100ml of 100ppm phenol solutions were taken and their pH maintained at 1, 4, 8, 10 and 12 respectively. HCl and NaOH were used to get the desired pH and a pH meter was used to measure the pH of the solution accurately. To these flasks the HCl activated adsorbent (0.25gm as optimum dosage) was added. The setup was then placed in a shaker for 24hrs. After 24hrs the amount of phenol left in the solution was checked by UV method. A graph of pH of solution vs. percentage of phenol removed was plotted. The procedure was repeated for the H_2SO_4 and H_3PO_4 activated adsorbents.

3. Effect of temperature

Five flasks with 100ml of phenol having concentrations 20ppm, 40ppm, 60ppm, 80ppm, 100ppm for each of the activated adsorbents were taken. To these 0.25gm of adsorbent was added. The setup was placed in a temperature controlled shaker for 24hrs to achieve equilibrium at a set temp of 20℃. After 24hrs, amount of phenol left in the solution was checked by UV method. A graph of concentration of solution vs. percentage of phenol removed was plotted. The process was repeated at temperatures of 30℃ and 40℃.

4. Effect of adsorbent dosage

100ml of 100ppm phenol solution was added to each of fifteen conical flasks. To these, a varying quantity of each adsorbent i.e. 0.1gm, 0.2gm, 0.3gm, 0.4gm, 0.5gm (activated adsorbent) was added. The pH of the solutions was adjusted according to data obtained from previous parameters. The setup was placed in a controlled-temperature shaker for 24hrs to achieve equilibrium. After 24hrs, amount of phenol left in the solution was checked by UV method. A graph of adsorbent dosage vs. percentage of phenol removed was plotted.

Table 1 Calibration of phenol solution

Concentration (ppm)	Absorbance
20	0.405
40	0.658
60	1.221
80	1.498
100	1.849

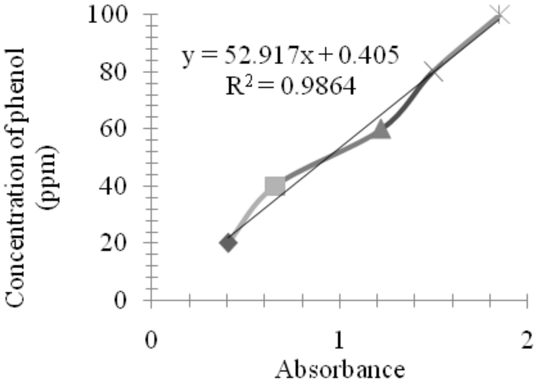

Fig. 1 Calibration graph

III. RESULTS AND ANALYSIS

A. *Test for effect of contact time*

In the cases of all three activated adsorbents, we observed that equilibrium was almost achieved within a period of 6 hours. There was a minor change in phenol concentration between 6 hours and 24 hours of contact time. An increase in initial phenol concentration resulted in a higher percentage of phenol removal. With the HCl activated adsorbent, a maximum phenol removal of about 77% was achieved, while H_2SO_4 activated adsorbent gave 84% and H_3PO_4 activated adsorbent removed 75% of the initial phenol concentration.

B. *Test for effect of temperature*

In accordance with findings available in literature [3], [14], [15] which state that temperature affects the adsorption rate by altering the molecular interactions and solubility of the phenol solution thereby increasing the active sites on the carbon surface; we observed that an increase in temperature resulted in an increase in the percentage of phenol removed from the solution.

C. *Test for effect of pH*

Phenol adsorption on activated carbon has been shown in previous literature [1], [12], [13] to be highest in a pH range of 2-6. Our tests agree with previous results with slight variations. The HCl-activated mango peel gave maximum phenol removal at a pH of 5.5. The H_2SO_4-activated adsorbent gave maximum phenol removal at a pH of 7 while the H_3PO_4-activated adsorbent worked best at a pH of 4. In a highly acidic solution, the presence of excess H^+ ions inhibits the formation of the phenoxide ion. Since adsorption requires phenol to form an ion in order to attach to the adsorbent surface, a very small amount of phenol gets adsorbed. In highly alkaline solutions, the negatively charged phenoxide ion has to compete against the excess OH^- ions to get adsorbed onto the positively charged surface of the activated carbon thus again resulting in low removal of phenol from the solution. Based on these tests, the pH of phenol solutions were adjusted during experiments according to the activated adsorbent used.

D. Test for effect of adsorbent dosage

We observed that an increase in the dosage of adsorbent resulted in a higher percentage of phenol removal. This was due to the availability of more active sites for phenol adsorption to take place; the adsorption of phenol being site specific [1]. However, a greater dose of activated carbon did not significantly increase the final percentage of phenol removed therefore, after the results of this test, we took the optimum dosage of activated carbon for all the experiments as 0.25g.

E. Kinetic Studies

a.) Pseudo-first-order kinetic model

The pseudo-first-order kinetic model used to predict adsorption kinetics is the model given by Langergren and Svenska which is defined as:

$ln\ (q_e - q_t) = ln\ q_e - k_1 t$

Where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (hr), respectively, and k_1 (1/hr) is the adsorption rate constant. The plot of $ln\ (q_e - q_t)$ versus t gives a slope of k_1 and an intercept of $ln\ q_e$ [2]. The readings obtained can be seen in Table 2.

Table 2 Pseudo-first-order kinetic model

	Conc (ppm)	k_1 (hr^{-1})	q_e (mg/g)	R^2
HCl	40	0.6628	15.502	0.8812
	60	0.4541	24.451	0.9765
	100	0.4444	28.960	0.8125
H_2SO_4	40	0.3240	15.951	0.9464
	60	0.3366	18.096	0.8928
	100	0.6420	16.158	0.6267
H_3PO_4	40	0.3788	13.064	0.9818
	60	0.3928	17.534	0.9825
	100	0.6641	25.043	0.9295

b.) Pseudo-second-order kinetic model

The pseudo-second-order equation based on equilibrium adsorption is expressed as:

$t/q_t = (1/k_2 q_e^2) + (1/q_e)t$

Where k_2 (g/mg h) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept. This procedure is more likely to predict the behaviour over the whole range of adsorption [2]. The readings can be seen in Table 3.

Table 3 Pseudo-second-order kinetic model

	Conc (ppm)	q_e (mg/g·min)	k_2 (g/mg·min)	R^2
HCl	40	76.923	0.000546	0.0875
	60	370.370	0.0000279	0.038
	100	88.495	0.0006397	0.0845
H_2SO_4	40	10.638	0.0095658	0.7676
	60	24.096	0.0158295	0.6101
	100	32.362	0.0691891	0.9852
H_3PO_4	40	38.610	0.0012697	0.0794
	60	25.575	0.0175121	0.9656
	100	33.333	0.037974	0.9831

Since the calculated correlations are closer to unity for the first-order kinetics model, the adsorption kinetics seems to be more favourably approximated by the first-order model.

F. Adsorption isotherms

An adsorption isotherm represents a relationship between the amount of adsorbate that has been adsorbed at a constant temperature and its concentration in the equilibrium solution. It provides physiochemical data for assessing the applicability of the adsorption process as a complete unit operation [17]. In our study, we assumed monolayer adsorption of phenol and applied the Langmuir and Freundlich isotherms to fit the equilibrium data of adsorption of phenol on activated carbon. The results obtained confirmed that our assumption was correct.

a.) Langmuir

The Langmuir isotherm is based on the assumption that adsorption takes place only at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate attaches onto a site, no further adsorption can take place at that site and therefore the adsorption process is monolayer in nature [14], [18].

The linear form of the Langmuir equation is:

$C_e/q_e = 1/(Q_0 b) + C_e/Q_0$

where C_e (mg/L) is the equilibrium concentration of phenol, q_e (mg/g) is the amount of phenol adsorbed per unit mass of adsorbent, and Q_0 (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A graph of C_e/q_e versus C_e would give a straight line having a slope of $1/Q_0$ and intercept of $1/Q_0 b$. The results are shown in Table 4.

Table 4 Langmuir isotherm

	Temp (°C)	Q_o (mg/g)	b (L/mg)	R^2
HCl	30	38.314	0.0390	0.8366
	40	44.843	0.0321	0.8439
H_2SO_4	30	46.512	0.0286	0.9910
	40	46.296	0.0280	0.9898
H_3PO_4	30	26.882	0.0501	0.7866
	40	17.123	0.1551	0.9068

b.) Freundlich

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface supporting sites of varied affinities. It is assumed that stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation [2], [19].

The linear form of the Freundlich equation is:

$log\ (x/m) = log\ k_f + (1/n)\ log\ C_e$

where x (mg) is the amount of phenol adsorbed and m (g) is the mass of adsorbent used, C_e (mg/L) is the equilibrium concentration of phenol in the solution, k_f ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$) and n are Freundlich constants. A plot of $\log (x/m)$ versus $\log C_e$ gives a straight line having a slope $1/n$ and an intercept of log k_f. The results obtained are given in Table 5.

Table 5 Freundlich isotherm

	Temp (˚C)	N	k_f ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$)	R^2
HCl	30	1.535	2.2972	0.8594
	40	1.460	2.1702	0.9593
H_2SO_4	30	1.411	1.9422	0.9873
	40	1.414	1.9111	0.9857
H_3PO_4	30	1.545	1.8471	0.7497
	40	2.150	2.9526	0.6643

IV. CONCLUSION AND FUTURE SCOPE OF WORK

A. *Work Conclusion*

The present investigation on mango peel as an activated adsorbent showed it to be satisfactorily employed for the tertiary removal of phenol from aqueous solutions.

The readily-available mango peel was activated with hydrochloric acid, sulphuric acid and phosphoric acid; Both H_2SO_4 and H_3PO_4 gave good results for the removal of phenol, however, better removal was achieved by H_2SO_4 activation.

Adsorption of phenol was found to increase with increase in agitation time (upto equilibrium) and initial concentration of phenol.

A pH of 7 was more favourable for the adsorption of phenol using mango peel activated by H_2SO_4, while a pH of 4 was better suited to removal by H_3PO_4 activation.

Equilibrium data was fitted to models of Langmuir and Freundlich; equilibrium data was best described by the Langmuir isotherm model indicating single layer chemisorption. Kinetic data was tested using the pseudo-first-order and pseudo-second-order kinetic models. The kinetics of the adsorption process was found to follow the pseudo-first-order kinetic model suggesting that pore diffusion was the rate limiting step.

FTIR analysis was conducted on the prepared activated carbon before and after phenol adsorption to study the surface chemistry of the activated carbon. The readings obtained showed an increase of peaks in the region 3100-3000 cm^{-1} (C–H, Phenyl ring substitution bands) showing the adsorption of phenol onto the surface of the adsorbent. The increase in peaks observed at 1581.52 cm^{-1} (C=C, Aromatic rings) confirm the adsorption of phenol. Peaks are also observed between 3600-3200 cm^{-1} (O–H, Hydrogen bonded phenol).

The BET surface area for the unactivated mango peel was $9.61 m^2/gm$. Surface area after activation was found to be the highest for H_2SO_4 activated mango peel with a surface area of 64 m^2/gm and a pore volume of 0.0628 cm^3/gm.

B. *Future Scope of Work*

Removal of phenol using activated carbon prepared from agricultural waste has a lot of prospect. Few agricultural wastes have already been studied such as that in this project (mango peel) and there are many more that are yet to be tested. Mango peel is a readily available agricultural waste with very few uses. Implementation of mango peel to remove phenol is a viable option and there is a lot of scope for improving its efficiency by finding a better activating agent and better methods of preparation.

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