Treatment of Phenolic Water Using Watermelon Seeds

Santosh A. Malunjkar, Kavita R. Ambekar

Abstract— **Phenolic compounds are found in wastewaters of various industries like as pulp and paper, coal conversion, plastics, iron, steel as well as petroleum. It is very important to removal of phenol from contaminated water before discharging into any natural bodies because of its toxicity to aquatic life. In the present study the adsorbent was prepared from the seed of Citrullus Lanatus (watermelon) obtained from local area. The adsorbent was activated by using activating agent and characterized SEM, BET surface area, etc. The effectiveness of the adsorbent is measured by finding out the concentration of phenol in the treated solution by use of UV-Spectrophotometer. The equilibrium data of phenol showed good correlated to Freundlich isotherm models. Adsorption kinetic data represents to the pseudo-second-order kinetic model. The maximum uptake capacity of phenol on to CLAC (Citrullus Lanatus Activated Carbon) was found 38.20 mg/g at 32° C. Also the following parameters of adsorption have been studied:- effect of contact time and initial phenol concentration, effect of pH, effect of temperature, effect of adsorbent dose. Taguchi experimental design was used to optimize the process variables of CLAC-phenol system.**

Index Terms- **Adsorption, CLAC, Phenol removal, Taguchi.**

I. INTRODUCTION

The toxic and hazardous nature of phenols and their derivatives have been well documented (Denizli et al., 2004). The high concentration discharge of these compounds in water receiving bodies and their exposure over a long period can cause severe impact on environment. The exposure of phenol and its derivative compounds to human and animals causes liver and kidney damage, central nervous system impairment, diarrhea and excretion of dark urine.

Several treatment methods are available for treating organic and inorganic waste including reverse osmosis, anaerobic process, biological degradation, membrane separation (Busca et al, 2008). All of these are used for treating organic and inorganic waste. Most of these methods suffer from some drawbacks, such as high capital and operational cost, regeneration cost, and problem of residual disposal. Liquid phase adsorption has been Shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, adsorbent cost, effectiveness and the availability of a wide range of adsorbents.

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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 and activation of adsorbent

The chars derived from seeds of Citrullus Lanatus (CL) wastes have been produced in a pyrolysis reactor. The seeds waste material. It was washed 5-6 times in running tap water and then with distilled water to remove the impurities. Then it was soaked in 2 M *HCl* solutions for two days and soaked material was sun dried for 24 hrs. The pyrolysis was carried out under the absence of air and in the conditions of heating rate 20° C /min, temperatures 600° C. The reaction was started at 436° C and it would take only 15 to 20 minutes to complete. The char was allowed to cool naturally in reactor. The char was crushed to a desired 100 BSS sieve size particle. The resultant char was then washed with distilled water until the pH of washed water was become neutral.

B. Reagents and Equipments

All necessary chemicals used in the study were of AR grade. The characterization of adsorbent was carried out for surface area analysis. Scanning electron microscope (SEM) study was conducted to observe the surface texture and porosity of the adsorbent. UV-spectrophotometer was used for determination of phenol content in standard solution and treated solution. The PH of the solution was measured by pH Meter.

C. Preparation Of Phenol Standards

The stock solution containing 1000 mg/l of standard Phenol was prepared by dissolving 0.25 g of AR grade Phenol in 100 ml double distil (DD) water. After dissolution both the solutions were diluted to 250 ml with DD water in 250 ml volumetric flask. Batch adsorption experiments were performed after proper dilution of stock solution. From this 50ppm, 100ppm, 150ppm, were made by pipetting out 5ml, 10ml, and 15ml solution respectively into 100 ml 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 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.

E. Effects Of Varying Parameters On Adsorption
Following are the methods for determining how various parameters affect adsorption

1. Effect of pH
Five flasks having 100ml of 100ppm phenol solution were taken and their pH maintained 2, 4, 6, 8, 10, and 12 respectively. HCl and NaOH were used to adjust PH in desired range and pH meter used to measure the pH of solution accurately. Then 0.28 g adsorbent was added. Then the setup was placed in mechanical shaker at 120rpm for 24 hrs. After 24 hrs amount of phenol left in the solution was checked by UV Method.

2. Effect of contact time
50 ml Phenol solution of 50 mg/l and 0.15 g TCAC was added into the series of flasks to investigate the effect of contact time and equilibrium time and then agitated at 120rpm for different time interval ranging from 15 min to 1440 min until the steady state reached.

The effect of initial concentrations for phenol onto TCAC were also studied for different concentrations of phenol 50, 100 and150 mg/l solutions at optimum pH of 5.7 and then treated as the procedure in the first experiment until equilibrium reached. All solution samples were filtered through Whitman 0.45μm filter paper. The concentrations of phenol in treated samples were determined by UV spectrophotometer. The amount of phenol adsorbed per unit mass of the adsorbent was evaluated by using the following equation.

$$q_e=(C_0-C_t)v/m \text{-----------------------------------}(1)$$

Percentage removal of phenol was calculated as follows,

$$\%removal = (C_0-C_t/C_0)100 \text{----------------------------} (2)$$

Where, C_0-intial concentration of phenol
C_t- final concentration of phenol
v- Volume of the solution in ml of adsorbate
m- Dose of CLAC in g.
A Graph of maximum uptake capacity vs contact time at different initial concentration.

3. Effect of temperature
The analysis of surface loading with increase in temperature, Phenol solution was prepared in five different conical flasks with phenol concentration (50, 100, 150, 200, 250 mg/l) and Adsorbent dose (2.8g/l and put inside the water bath shaker. The temperature was maintained at 30˚ c. The final Phenol concentration was measured after 24 hours. The similar experiments were conducted for temperatures 40˚C, 50˚C and 60˚C. A plot of uptake capacity of TCAC against time at different temperatures was plotted.

4. Effect of adsorbent dosage
In order to study the effect of adsorbent dosage, different dosages of CLAC were varied from 1 to 7 g/l, and were placed into series of the 100mL flasks of Phenol solution (100mg/l). These were agitated for 24 h at 120 rpm at the neutral pH. The amount of phenol left in the solution was checked by UV method. A graph of adsorbent dosage vs %

removal and adsorbent dosage (g/100ml) vs maximum uptake capacity (mg/g) plotted.

III. RESULTS AND ANALYSIS

A. Test for effect of pH
The effect of initial pH on the adsorption of phenol was also evaluated at 305K at different initial pH values in the range of 2–12 for initial concentrations of 100ppm for phenol solution by adding 0.1M HCl or 0.1M NaOH. The HCL activated CLAC system gives optimum phenol removal at a pH 5.7 due to the mild increased in H+ adsorption on the carbonyl sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed as the pH increased from 10 to 13 is attributed to both greater solubility of dissociated phenol.
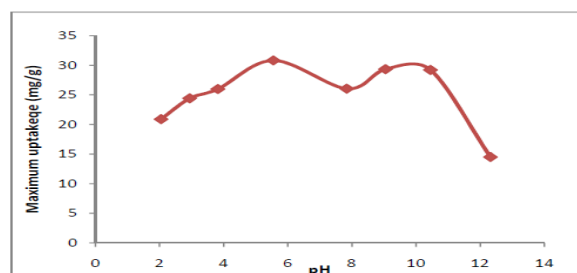

Fig. 1 Effect of adsorption capacity for 100ppm in 24 hrs at 32˚C

B. Test for effect of contact time and initial phenol concentration

The results also indicated that up to 50% of the total amount of phenol uptake was found to occur in the first (30min) and thereafter the rest 50% of maximum uptake was reached in 24 hours. The uptake capacity increased with increase in initial concentration, which may be due to the availability of more number of phenolate ion in solution for sorption. Moreover, higher initial adsorbate concentration provided higher driving Force to overcome all mass transfer resistances of the phenolate ions from the aqueous to the solid phase resulting in higher probability of collision between adsorbent and the active sites (srivastav et al., 2006). The higher sorption rate at the initial period (first 30min) may be due to an availability of large number of vacant sites on the adsorbent at the initial stage.

C. Test for effect of temperature

The value of maximum adsorption capacity qe decreases with temperature thus suggesting that adsorption is favored at lower temperatures. At high temperature kinetic energy of adsorbate phenol is so high that they do not bind with the active sites available on the TCAC surface. However if the process was endothermic in nature than only the sorption capacity would increase because of inter molecular pore diffusion (Weber, 1972).

D. Test for effect of adsorbent dosage

It was found that with increase in adsorbent dose the percentage removal increases indicating the presence of large surface area available for adsorption with decreasing the maximum adsorption capacity. Hence, the optimum dosage

was considered where these intersect Fig. 2 Hence, in all the experiments; 2.8 g/l was kept as an adsorbent dosage.
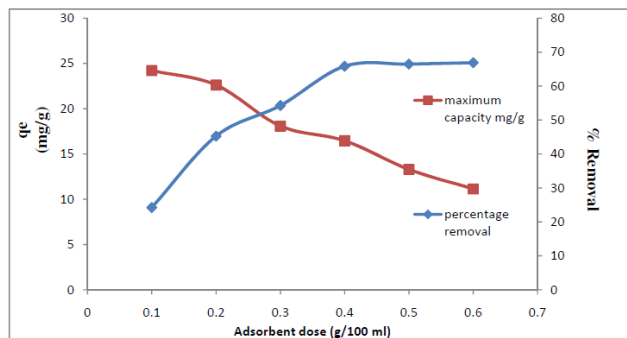

Fig. 2 Effect of adsorbent dose for phenol removal at pH (neutral) 100mg/l for 24 hrs at 32°C.

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:

$$ln(q_e - q_t) = ln\ q_e - k_1 t \text{-------------------------------- (3)}$$

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 $ln\ q_e$. The readings obtained can be seen in Table 1.

Table 1 Pseudo-first-order kinetic model

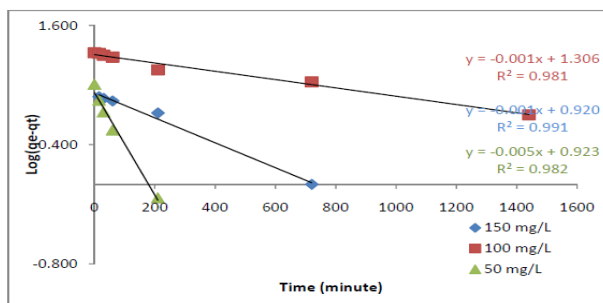| C_o (mg/l)	q_e (mg/g)	q_{cal}	k_f	R^2
50	11.4832	8.4217	0.0121	0.9842
100	17.1211	9.8521	0.0027	0.9817
150	25.7122	19.9321	0.0026	0.9940

Fig. 3 Pseudo-first- order kinetic plot for the phenol-CLAC system, (T=32°C, m=2.8 g/l)

b.) Pseudo-second-order kinetic model

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

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)\ t \text{----------------------------------(4)}$$

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 behavior over the whole range of adsorption. The readings can be seen in Table 2.

Table 2 Pseudo-second-order kinetic model

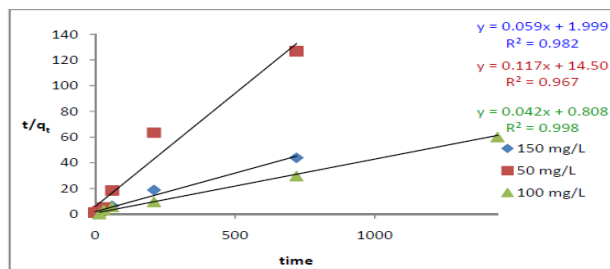| C_o (mg/l)	q_e (mg/g min)	K_2 (g/mg min)	R^2
50	11.4832	0.0002	0.9679
100	17.1211	0.0017	0.9833
150	25.7122	0.0002	0.9969

Fig. 4 Pseudo-second-order kinetic plot for the Phenol-CLAC system (at 32°C, m=2.8g/l)

F. Adsorption isotherms

The several adsorption isotherm models like Langmuir, Frendulich have been used to test the equilibrium kinetics data. 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) Freundlich

It is assumed that stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation 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/g)/(mg/l)$^{1/n}$ 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 3

Table 3 Freundlich isotherm

Temp(°C)	k_f (mg/g)/(mg/l)$^{1/n}$	$1/n$	R^2
30	8.7320	0.2757	0.9905
40	5.7320	0.3316	0.9649
50	5.4211	0.3321	0.9746
60	6.2092	0.2869	0.9182

b) 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. The linear form of the Langmuir equation is:

$$C_e/q_e = 1/(q_m K_L) + C_e/q_m$$

Table 4 Langmuir isotherm

Temp(°C)	q_m (mg/g)	K_L (l/mg)	R^2
30	38.2012	0.0583	0.9894
40	37.8762	0.0376	0.9795
50	36.9230	0.0344	0.9742
60	32.1236	0.0409	0.9583

IV. CONCLUSION AND FUTURE SCOPE OF WORK

A. Work Conclusion

The present investigation on Citrullus Lanatus as an activated adsorbent showed it to be satisfactorily employed for the tertiary removal of phenol from aqueous solutions. Adsorption of phenol was found to increase with increase in agitation time and initial concentration of phenol.

- t=24 h, pH=5.7, Co=150 mg/l, T=32°C and m= 2.8 g/l were the optimum condition for Phenol-CLAC system.
- Maximum uptake capacity of phenol 38.2 mg/g.
- Equilibrium data was fitted to models of Freundlich isotherms.
- Adsorption of phenol is decreases with increase in the temperature indicating exothermic nature of the adsorption process.
- 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-second-order kinetic model.

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 Citrullus Lanatus (watermelon) and there are many more that are yet to be tested. Citrullus Lanatus (watermelon) is a readily available agricultural waste with very few uses. Implementation of Citrullus Lanatus (watermelon) 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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