Water Hyacinth (*Eichornia Crassipes*) as an Effective Biosorbent for sorption of Phenol

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ABSTRACT

In present paper the sorption of phenol using low-cost water hyacinth activated carbon (WHAC) has been presented. The effect of various parameters such as pH, biosorbent dose, temperature, initial phenol concentration and contact time were studied and optimized. The optimum biosorbent dosage, equilibrium contact time, and pH were found to be 5 g/l, 350 min, and 6 respectively. The entropy change and heat of sorption for phenol-WHAC system were estimated as 40.85 kJ/mol K and -27.81 kJ/mol, respectively. The sorption of phenol onto WHAC was found to be exothermic in nature. The negative value of Gibbs free energy indicates the spontaneousity nature of phenol sorption onto WHAC..

1. Introduction

The presence of phenol can commonly be observed in various industrial effluents with different concentration (Li et al., 2012; Guido et al., 2008). Phenols are considered as priority pollutants with various harmful effects on human and aquatic life (Keith and Telliard, 1979; Srivastava et al., 2006). Therefore, the removal of phenol from the wastewaters is very necessary before their safe disposal to the aquatic environment. Several regulatory bodies all over the world have set the maximum permissible limits of phenol in wastewater, drinking water and industrial effluent. The US Environmental Protection Agency (USEPA) with a permissible limit of 0.1 mg/l in wastewater, the Ministry of Environment and Forests (MOEF), Government of India has set a maximum concentration level of 1.0 mg/l of phenol in the industrial effluents for safe discharge into surface waters, the World Health Organisation (WHO) and Bureau of Indian Standards (BIS) recommends the permissible phenolic concentration of 1.0 µg/l in potable waters. (Kumar et al., 2012).

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Several techniques like advanced oxidation, membrane filtration, biological degradation, electrochemical oxidation, photocatalytic degradation and adsorption are employed for removal of phenol from aqueous media (Srivastava et al., 2006; Guido et al., 2008; Li et al., 2012). The biosorption has been considered as one of the most-widely used technique for treatment of phenolic wastewaters for high strength and low volume of phenolic wastewaters due to its low cost and high efficiency. In the past few decades, various low cost biosorbents have been used to remove phenols from aqueous solutions (Ahmaruzzaman, 2008).

There are several materials available in abundance for the preparation of low cost biosorbents (Singh et al., 2006; Singh et al., 2008). Very few literatures are available on the treatment of phenolic wastewater using WHAC. In view of this, the water hyacinth (Eichornia crassipes) was used to prepare water hyacinth activated carbon (WHAC) for removal of phenol from wastewater. The sorption of phenol was studied through various experimental parameters such as biosorbent dosage, pH, contact time, initial concentration, and temperature. The thermodynamic parameters were also evaluated using experimental data to elucidate the nature of phenol sorption onto WHAC.

2. Materials and methods

2.1. Biosorbent and Adsorbate

The biosorbent was prepared as per the procedure given by Dash et al. (2010). The physicochemical characteristics of prepared WHAC are presented in Table 1. The stock solution was prepared by dissolving 1.0 g of AR grade phenol (Merck) in 1000 ml double distilled water (DDW). The test solutions of desired concentrations were prepared by diluting the stock solution. The pH of the samples were adjusted with 1N H2SO4 and 1N NaOH solutions.

2.2. Analytical Measurement

The standard calibration curve of known concentration of phenol was plotted using spectrophotometer (Model: JASCO UV/Vis-530) with absorbance at = 270 nm (Khare and Kumar, 2012) which shows a linear variation up to 100 mg/l concentration. Therefore, the samples of higher concentration of phenol were subsequently diluted with DDW. The standard calibration curve of phenol concentration was used to find out the unknown concentration of phenol in various samples.

2.3. Physicochemical analyses

The batch sorption experiments were performed in a temperature controlled water bath mechanical shaker at constant speed of 120 rpm using 100 ml conical flasks containing 50 ml phenol solutions each. Post sorption solution samples were filtered through syringe driven Millipore Whatman (0.45μm) filter paper. The concentrations of phenol in treated samples were determined by UV spectrophotometer as mentioned earlier.

The amount of phenol adsorbed per unit mass of the biosorbent at equilibrium was evaluated as:

$$q_e = (C_o - C_t)\frac{V}{m} \qquad (1)$$

The percentage removal of phenol was calculated as:

$$\%R = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \qquad (2)$$

Where Co the initial phenol concentration (mg/l) is, V is the volume (ml) of the wastewaters in the flask, Ct is the phenol concentration (mg/l) after time and m is the initial mass of the WHAC (g).

Table 1: Physico-chemical characterization of WHAC

Characteristic	**value**
Proximate analysis (sample as received)	
Moisture (%)	5.85
Ash (%)	8.026
Volatile matter (%)	17.43
Fixed carbon (%)	68.70
Bulk density (kg/m^3)	285.51
pH_{PZC}	6.80
Heating value (MJ/kg)	27.23
Ultimate analysis (dry basis) (%)	
C	70.23
H	5.40
N	4.96
S	-
Surface area (m^2/g)	
BET	607.64
Langmuir	1485.60

3. Results and discussion

3.1 Effect of adsorbent dose

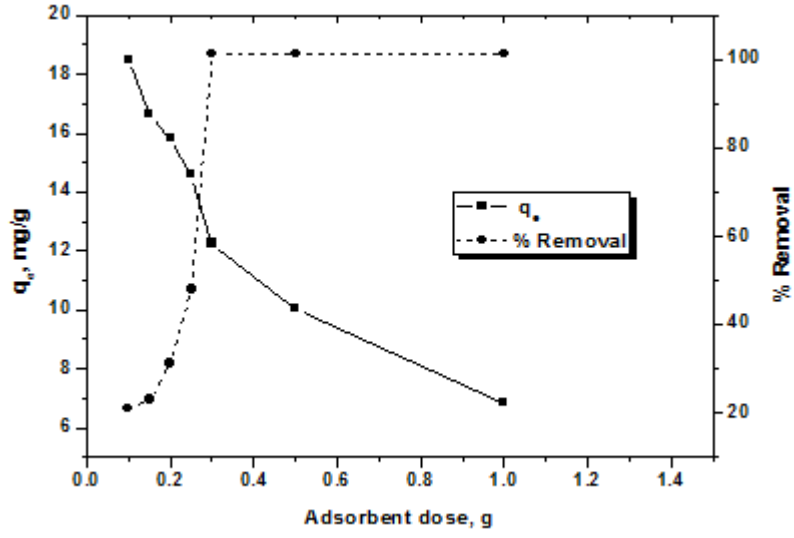

Fig. 2 Effect of biosorbent dosage on the removal of phenol by WHAC (C_o = 100 mg/l, pH_o =natural, T = 303 K, t = 24 h).

The effect of biosorbent dosage (m) on the uptake of phenol by WHAC was studied for = 100 mg/l. It is found that the removal of phenol increased with increased in the biosorbent dose (Fig. 1). However, the uptake capacity of phenol decreases with increase in biosorbent dosage. At the print where these two curves meet is the optimum dosage of WHAC. The removal of phenol remains almost constant with a removal efficiency of ~100 % for 0.3g for WHAC. The sorption of phenol is enhanced with an increase in the biosorbent dosage, because of availability of larger surface area and sorption sites. At lower dosages of the biosorbents, the biosorbent surface becomes saturated with phenol and a larger residual phenol concentration remains in the solution. At a dosage of 0.3g of WHAC for = 100 mg/l, equilibrium conditions exist for the phenol–WHAC system with almost no increase in the phenol uptake. (Table 1).

3.2 Effect of pH

The effect pH in the range of 2–12 on phenol uptake is illustrated in Fig. 2. The surface charge of carbon depends on the solution pH and its pH_{PZC}. The carbon surface is positively charged at pH< pH_{PZC} and negatively charged at pH>pH_{PZC}. Due to this reason the uptake of phenol was observed in both the medium (Khare and Kumar, 2012). At pH=6 highest uptake was observed because of the dissociation of phenol into negatively charge phenolate ion.

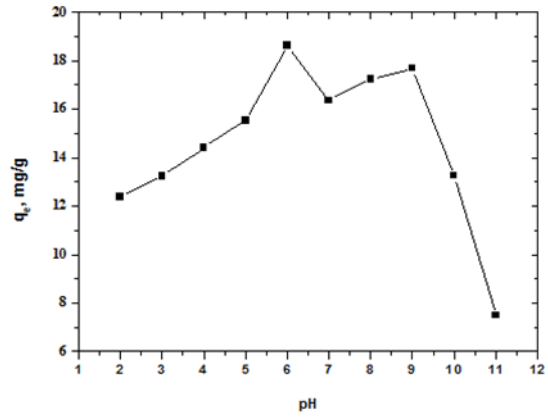

Fig. 2 Effect of pH on the sorption of phenol by WHAC (T = 303 K, t = 350 min, C_o = 100 mg/l, m_{opt} = 5 g/l).

3.3 Effect of contact time and initial concentration

The effect of contact time on the sorption of phenol uptake (q_e) of WHAC is shown in Fig. 3. It is found that the equilibrium sorption time is ~350 min. This is obvious from the fact that a large number of vacant surface sites are not available for the sorption during the initial stage and with the passage of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase. The effect of initial concentration (C_o) on the extent of sorption for Phenol-WHAC system as a function of time is shown in Fig. 4. At any time, q_e is increased with increased in C_o. However, the biosorption rate is decreased. The C_o provides the necessary driving force to overcome the resistance to mass transfer of phenol between the aqueous phase and the solid phase. The increase in C_o also enhances the interaction between phenol molecules and the vacant sorption sites on the biosorbent and the surface functional groups.

Therefore, an increase in C_o enhances the uptake of phenol.

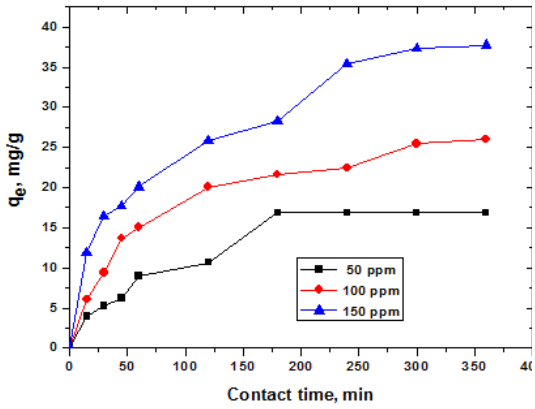

Fig. 4 Effect of contact time and initial concentration on the sorption of phenol by WHAC (m_{opt} = 5 g/l of WHAC, T = 303 K, pH_o= 6).

3.4 Effect of temperature on sorption of Phenol onto WHAC

To elucidate the effect of temperature on phenol uptake, the solutions of different concentrations of phenol ranging from 50 mg/l to 250 mg/l were prepared. All sample solutions were maintained at initial pH of 6 and 5 g/L WHAC was added to each sample, then all the samples were agitated for 6 hours at different temperatures 30, 40, 50, and 60 ^oC respectively. Uptake capacities of WHAC against initial concentrations at different temperatures are shown in Fig.5. It is evident from Fig. 4 that the value of uptake q_e decreases with increase in temperature suggesting that phenol uptake is favored at lower temperatures. At high temperature kinetic energy of phenol molecules is so high that they do not bind with the active sites available on the WHAC surface. It can, therefore, be inferred that the sorption of phenol is exothermic in nature.

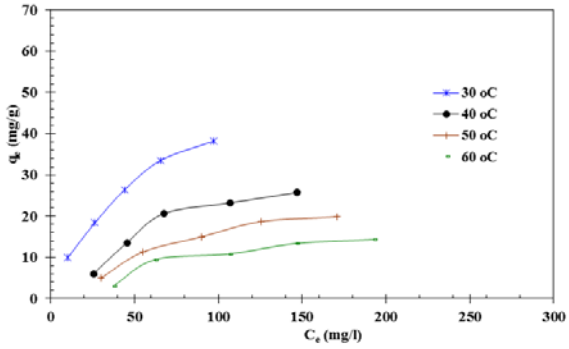

Fig. 5 Equilibrium isotherms for the sorption of phenol onto WHAC at different temperatures. (t = 350 min, m_{opt} = 5 g/l, pH_o= 6).

4 **Adsorption equilibrium study**

To study the applicability of the Langmuir, Freundlich, Tempkin, Redlich-Peterson and D-R isotherms for the phenol adsorption onto WHAC, plots of q_e versus C_e were plotted, and the values of $K_F, 1/n, q_m, K_L, K_T, q_s, E, K_R, a_R$, and R^2 (correlation coefficient values of all isotherms models) are shown in Table 2. The correlation coefficient values (R^2) show that the phenol removal isotherm using WHAC does not follow the Langmuir, Freundlich Redlich-Peterson and D-R isotherms (Table 2). The calculated correlation coefficients for Tempkin isotherm model show that the phenol removal isotherm can be approximated as the Tempkin model (Table 2). This means that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions.

Table 2. Isotherm parameters and error analysis for the removal of phenol-WHAC system

Freundlich

Temp. (^oC)	K_F [(mg/g)/(mg/l)$^{1/n}$]	1/n	R^2
30	2.4431	0.6158	0.9960
40	0.5435	0.8066	0.9470
50	0.4062	0.7845	0.9649
60	0.1909	0.8516	0.9092

Langmuir

Temp. (^oC)	q_m	K_L	R^2
30	60.0800	0.0182	0.9948
40	62.0143	0.0054	0.7848
50	46.6915	0.0049	0.8635
60	45.8342	0.0027	0.5252

Temkin

Temp. (^oC)	K_T	B_1	R^2
30	0.1890	12.8910	0.9901
40	0.0732	11.3594	0.9827
50	0.0627	8.6897	0.9940
60	0.0523	6.4579	0.9648

D-R

Temp. (^oC)	q_s (mg/g)	B	E (KJ/mol)	R^2
30	30.6505	-2.11E-05	0.153785487	-0.9178
40	25.0345	-0.000146	0.058561936	-0.9896
50	18.9778	-0.000176	0.053344053	-0.9879
60	14.7783	-0.000287	0.041742076	-0.9907

Redlich-Peterson

Temp. (^oC)	K_R	a_R	β	R^2
30	1.9833	0.2661	0.5821	0.9958
40	1.292406813	1.6251	0.2334	0.5678
50	14.18406813	34.1717	0.2178	0.7100
60	121.429432	635.0166	0.1486	0.3556

Table 3. Thermodynamic parameters for the sorption of phenol onto WHAC

	Phenol-WHAC
ΔG^o (kJ/mol)	
$30\,^oC$	-14.41
$40\,^oC$	-19.78
$50\,^oC$	-110.56
$60\,^oC$	-120.78
ΔH^o (kJ/mol)	-27.81
ΔS^o (kJ/mol K)	40.85

5. Thermodynamics of biosorption

The biosorption thermodynamics were studied and parameters including Gibbs free energy change , enthalpy change and entropy change were estimated according to following thermodynamic equations

$$\Delta G^o = -RT\ln K \quad (3)$$

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (4)$$

Where K (L/mol) is from Langmuir equation, R is the gas constant (8.314 J/mol K) and T is the temperature in Kelvin. In the application of Eq. (4), the values of ln K are plotted against 1/T and the ΔH^o and ΔS^o values are calculated from the slope and intercept of the plot. The value of ΔH^o for phenol-WHAC system was found to be −27.81 kJ/mol indicating that the sorption of phenol onto WHAC is exothermic in nature. The positive value of ΔS^o (40.85 kJ/mol K) suggests an increased randomness at the solid–solution interface. The values of thermodynamic parameters estimated are presented in Table 3. A negative value of ΔG^o suggests that the sorption of phenol is spontaneous and exothermic in nature (Senturk et al., 2009; Dash et al.,2010; Muftah et al., 2010).

6. Conclusions

- WHAC is an effective biosorbent for the removal of phenol from aqueous solution.
- Higher uptake of phenol was possible provided that the C_o in the solution was high.
- Optimum conditions for phenol removal were found at $pH_o \approx 6$ and biosorbent dose 5 g/l. The equilibrium between the phenol in the solution and on WHAC surface was achieved in 350 min.
- Sorption of phenol on WHAC is favorably influenced by a decrease in the temperature of the operation.
- The negative value of Gibbs free energy indicates spontaneous sorption of phenol onto WHAC.

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