KINETICS AND EQUILIBRIUM STUDY OF ADSORPTION OF PHENOL RED ON TEFF (*Eragrostis teff*) HUSK ACTIVATED CARBON

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ABSTRACT: It has been widely recognized that dye removal by activated carbon adsorption is due to the surface action between the dye and the functional groups present in the surface of the carbon. This work presents a systematic experimental study on kinetics and equilibrium of adsorption of phenol red (PR) on teff (*Eragrostis*) husk activated carbon (THAC) and husk powder (HP). The adsorbents were characterized by using X-ray diffraction and Fourier transform infrared spectrometric techniques to understand the effect of surface properties on the adsorption of phenol red. The adsorption process was optimized with respect to pH, adsorbate initial concentrations, adsorbent dosage and contact time. Based on the results obtained, it was shown that teff husk activated carbon was more effective adsorbent than teff husk powder. The maximum adsorption of PR dye on THAC and HP occurred at pH of 5.2 and 5.0, respectively. Kinetic parameters of adsorption such as the Lagergren rate constant and the intraparticle diffusion rate constant were also determined. The calculated values of the amount of dye adsorbed per gram of adsorbent at equilibrium (qe) using pseudo second order equation were in good agreement with the corresponding experimental values. The observed negative value of Gibbs free energy of adsorption (ΔG_{ads}) indicates that the adsorption process is spontaneous and the positive enthalpy of adsorption (ΔH_{ads}) as well as entropy of adsorption (ΔS) show that entropy gain is the driving force rather than the energy change for the adsorption of phenol red on the THAC and HP.

KEYWORDS: Adsorption, Activated Carbon, Equilibrium, Isotherm, Thermodynamic.

1   INTODUCTION

Industrial effluents are one of the major causes of environmental pollution. Effluents discharged from dyeing industries are highly coloured with a large amount of suspended organic solids. Untreated disposal of this coloured water into the receiving water body causes damage to aquatic life as well as to human beings by their mutagenic and carcinogenic effects. The discharge of such effluents is worrying for both toxicological and environmental reasons [1].

Activated carbon is the most popular adsorbent for the adsorption process since it has high adsorption capacity. The adsorption capacity of activated carbon depends not only on its surface area, but also on its internal pore structure, surface characteristic and the presence of functional groups on pore surface. Internal pore structure and surface characteristic play an important role in adsorption processes and depend both on the precursor used and method of preparation. Different methods such as small angle X-ray, mercury porosimetry, scanning electron microscopy and gas as well as liquid phase adsorption are available for characterizing the pore structure (surface area, pore volume, pore size distribution, etc.) of

activated carbon [2]. The characteristics of adsorption behaviour of activated carbons are generally inferred in terms of both adsorption kinetics and equilibrium isotherm. Though most widely used adsorbent for this purpose is activated carbon, yet commercially available activated carbons are expensive and may not be economical for large scale wastewater treatment [3]. Other untreated low-cost adsorbents often have low adsorption capacities; therefore, their adsorbate removal efficiencies are poor. If an activated carbon with high adsorption capacity for wastewater treatment can be produced from low cost or waste materials, such as an adsorbent then the adsorption process may be economical as well as a means to minimize its waste disposal problem [4]. Thus, the present study was designed on the assumption that teff husk can be used as a potential low cost adsorbent if investigated, for its dye removal capacity from waste water both as an activated carbon form and as its non activated form.

2 METHODS

Teff husk was collected from local markets. The husk was washed with distilled water and sun dried for a day followed by drying at $100\,^0$ C to a constant weight for 24 hours. The dried material was mixed with equal amount of conc. H_2SO_4 and kept at room temperature, overnight. Excess of the acid was removed by washing the solid residue with distilled water till it attained neutral pH, and then soaked in 2 % $NaHCO_3$ solution overnight in order to remove excess acid present if any and the product was air-dried at room temperature. The material thus prepared was kept in hot air oven at $120\,^0$ C for 10 hours and then transferred to a muffle furnace kept at $500\,^0$ C for an hour. The dry product thus obtained was crushed in to granules and fractionated into different mesh sizes and then preserved in desiccators for further use.

2.1 PREPARATION OF PHENOL RED (PR) SOLUTIONS

A 0.01 M stock solution of phenol red was prepared by dissolving its appropriate amount in 250 mL distilled water. Different concentrations of PR ranged from 0.003 – 0.007 M were prepared from the stock solution. Double distilled water was used for preparing different solutions and reagents. All the adsorption experiments were carried out at room temperature.

2.2 ADSORPTION STUDIES

250 mL of phenol red dye solution was mixed with fixed amount of adsorbent (0.01 g) in a 500 mL conical flask. It was shaken at room temperature. Five mL each sample was collected at a regular interval of time centrifuged and filtered. Absorbance of filtrated was recorded on UV/Visible spectrometer, and concentration of dye was obtained from Absorbance *versus* Concentration curve. The amount of dye adsorbed per gram of adsorbent (qe) was calculated using the following equation:

$$qe = \frac{C_o - C_e}{W} V \qquad (1)$$

Where, Co and Ce are the initial and equilibrium concentrations of the adsorbate (phenol red dye), respectively; V = volume of dye solution and W = weight of adsorbent.

2.3 ADSORPTION ISOTHERMS

Batch adsorption experiments were carried out using rotary shaker at 150 rpm in 200 mL shaking flasks at room temperature for 50 min. The adsorbent was thoroughly mixed with 250 mL of PR solution. The isotherm studies were performed by varying the initial PR concentrations as 0.003, 0.004, 0.005, 0.006 and 0.007 M at pH 2.5, which was adjusted using 0.1M HCl or 0.1 M NaOH before addition of the adsorbent. After shaking the reaction mixture, it was analysed for the residual PR concentration.

2.4 SPECIFIC SURFACE AREA OF CARBON

Surface area per gram of the activated teff husk carbon was obtained using Sears method [5]. A 1.5 g of carbon sample was mixed with 100 mL of water and 30 g NaCl. The mixture was stirred for five minutes. To this 0.1 N HCl was added to make a final volume of 150 mL and final pH of 4.0. It was then titrated against 0.1 N NaOH. The volume of 0.1 N NaOH required to raise the pH from 4.0 to 9.0 was noted. The specific area (i.e. area per gram) was obtained using the formula:

$$A = 32.V - 25 \qquad (2)$$

Where A= surface area of adsorbent (activated carbon) per gram (in m^2/g); V = volume of 0.1 N NaOH required to raise the pH from 4.0 to 9.0.

3   RESULTS AND DISCUSSIONS

Physico-Chemical Parameters of Adsorbents

Table 1. Physico-chemical parameters of teff husk powder and its activated carbon.

Property	Husk powder	Activated carbon
Bulk density (g/cm^3)	0.4225	0.5416
Moisture content (%)	9.89%	2.04 %
Ash content (%)	7 %	9.12 %
pH	7.41	10.5
Pzc	7.1	8.71
Specific Surface area (m^2/g)	263	295

Physico-chemical parameters of activated carbon and husk powder are recorded in Table 1. Low moisture content of activated carbon ensures availability of more active sites on it and better adsorption efficiency. Carbon with higher moisture content demands the use of additional weight of carbon during treatment processes [6]. Ash content levels of activated carbon were higher than the husk powder, suggesting higher inorganic constituent in the former. The carbon having little amount of ash content may remove the inorganic contaminants effectively [7].

Activated carbon with higher bulk density is more suitable for the adsorption treatment process compared to low density carbon that suspends on water. Thus, providing poorer adsorbate - adsorbent contact. Also the lower bulk density values illustrates that the carbon samples are highly branched and porous with more void space [8]. Activated carbon which has higher specific surface area than husk powder, therefore the activated carbon can remove the phenol red dye from aqueous solution more effectively. Activated carbon has higher pH than husk powder because when a substance carbonized its basicity increase when treated with NaHCO$_3$ solution.
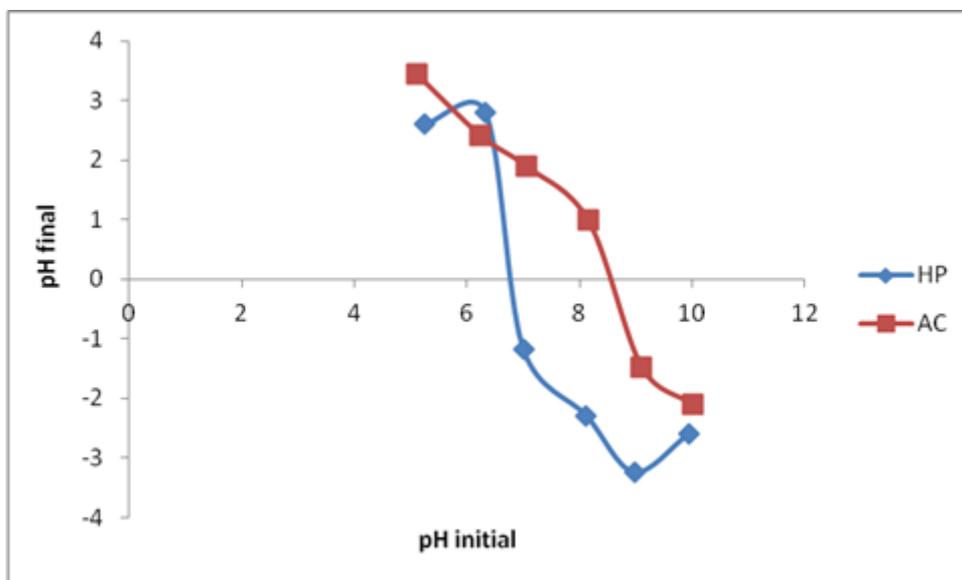
Figure 1. Determination of point of zero charge of the sorbents.

The zero point charge implies that the prepared carbon is free from surface charges nearby neutral pH. Hence the carbon samples are suitable for the treatment of water even at the neutral medium. The value of pH affected a net zero charge on a solid, in the absence of specific biosorption, is called the pHpzc. When the pH of the aqueous solution is below the pHpzc, the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively

charged when the solution pH is greater than pHpzc [9]. pHpzc for husk powder and activated carbon are 7.1 and 8.71, respectively.

Figure 2. Plot of amount of phenol red adsorbed per gram of adsorbent (mol/g) as a function of time

It can be seen that sorption efficiency of phenol red increases with the increase of time up to 30 min using activated carbon but in husk powder increases up to 40 min. In activated carbon, after definite time equilibrium between the rate of adsorption and rate of desorption become equal and there is no further net adsorption of the adsorbate [10].

Figure 3. XRD of teff husk activated carbon (THAC)

The obtained XRD spectra (Figure 3) of teff husk activated carbon exhibited no diffraction peaks. It suggests an amorphous structure of the synthesized teff husk carbon. The small peaks indicate the contaminants which are present in the activated carbon.
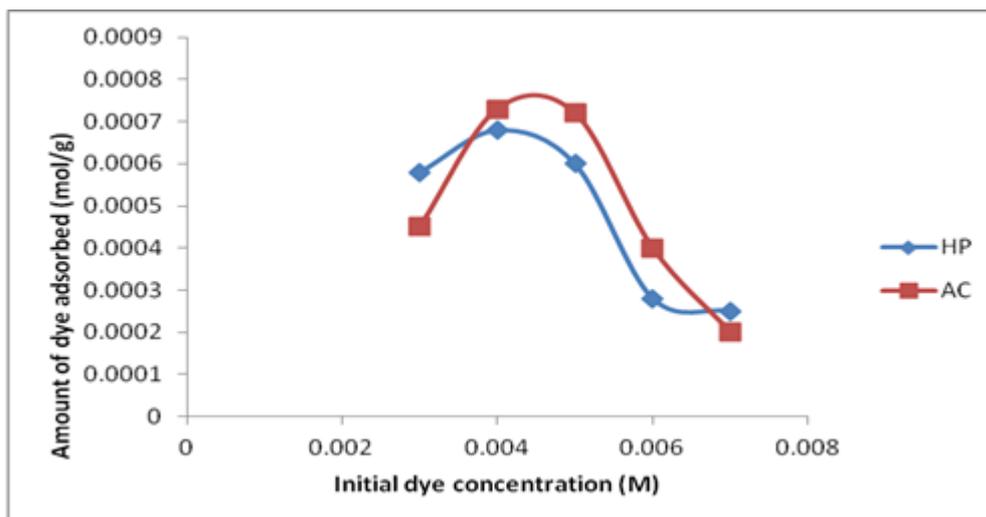
Figure 4. Plot of amount of phenol red adsorbed per gram of adsorbent (mol/g) on to THAC and HP (adsorbent dose = 0.01 g/L, pH = 7, and Agitation speed = 140 rpm).

Initially the removal of dye increased with the increase of dye initial concentration, and maximum removal of dye was using its initial concentration 0.005 M. This may be due to availability of more active sites per dye molecule [11]. In case of low concentrations, the ratio of the initial number of moles of solutes to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent and consequently higher adsorption yields were obtained. However, at higher concentration, most of the adsorption sites could be occupied by phenol red and the available sites of adsorption would become fewer, hence the removal of dyes which depends up on the initial concentration decrease [12]. The maxima of such plot shift to higher dye initial concentration in case of activated carbon as adsorbent.

4   CONCLUSIONS

In this study, activated carbon prepared from teff husk has been used successfully, as an efficient adsorbing agent for the removal of phenol red dye from aqueous solutions. Effects of operational parameters such as solution pH, adsorbent concentration, dye initial concentration, and contact time that governs the overall process of adsorption, have been investigated, X-ray diffraction pattern indicated that the synthesized adsorbent has amorphous structure. The amount of dye sorbed was found to vary with initial pH, adsorbent dose, phenol red concentration and contact time. The phenol red dye sorption decreased at high pH values in accordance with a presupposed ion-exchange mechanism of the adsorption. Since teff husk is freely, abundantly and locally available, it can be used as an economical sorbent for treating real industrial effluent against dyes pollutants.

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