Coal Ash as a Low Cost Adsorbent for the Removal of Xylenol Orange from Aqueous Solution

Ishaq, Mohammad; Saeed, Khalid*+•; Ahmad, Imtiaz; Sultan, Sirraj
Institute of Chemical Sciences, University of Peshawar, Peshawar-25120, Khyber Pakhtunkhwa, PAKISTAN

Akhtar, Sohail
Depatrment of Statistics, University of Malakand, Chakdara, Dir (L), Khyber Pakhtunkhwa, PAKISTAN

ABSTRACT: *The removal of xylenol orange from aqueous solution onto the coal ash was investigated at room temperature. The results show that the adsorption capacity of xylenol orange increased as the adsorption time increased and then equilibrium established after 30 min adsorption time. The results obtained revealed that the coal ash removed about 80 % of xylenol orange from the aqueous solution within 40 min. The effect of pH also studied, which showed that the adsorption of xylenol orange on the coal ash decreased as pH increased. The equilibrium adsorption isotherm data was fitted in Langmuir and Freundlich model equation and was found that the data followed both Langmuir and Freundlich isotherm models. Furthermore, we used a statistical measure (rank equation) in order to measure the strength of the relationship between the adsorption of xylenol orange onto coal ash and different adsorption time, and adsorption of different concentration of dye at equilibrium time.*

KEY WORDS: *Xylenol orange, Coal ash, Kinetics, EDX.*

INTRODUCTION

The dye manufacturing and textile finishing industries discharge large amount of colored wastes into receiving stream especially in dyeing and subsequent rinsing steps. Most of these dyes and pigments show resistance for their biodegradation in waste water due to their large size, complex molecular structures and light stable, which upset the aquatic life. It is reported that the human eye can detect 0.005mg/L of reactive dye concentrations in water. The removal of coloring materials from waste water is important from environment point of view due to their synthetic origins and also the presence of aromatic structures. These dyes and pigments in waste water are non-oxidizable by conventional physical methods and also resist to biodegradation. It is due to their large size and complex molecular structures, and shows stability towards heat and light, which highly disturbs aquatic life [1-3]. The discharge of these coloring materials into the streams not only effect animals but also interferes with transmission of sunlight into streams, which reduces photosynthetic activity [2]. The conventional methods

* To whom correspondence should be addressed.
+ E-mail: khalidkhalil2002@yahoo.com
• Other Address: Department of Chemistry, University of Malakan, Chakdara, Dir(L), Khyber Pakhtunkhwa, PAKISTAN
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such as primary and secondary treatment are not suitable for the removal of coloring materials from industrial effluents [4]. It was reported that adsorption is the most effective method for the removal of dyes and pigments from industrials waste water [5]. Various research groups used different types of adsorbents such as bentonite, silica gels, fly ash, lignite, peat, silica, chitosan and chitin, pine saw dust, hydrazine modified polyacrylonitrile etc. for the removal of toxic materials like dyes, metal ions and other organic materials from the wastewater [6-15].

In this study, coal ash is used as an adsorbent for the removal of xylenol orange from aqueous solution. The xylenol orange is used as an adsorbate because it causes eye and skin irritation, gastrointestinal irritation with nausea, vomiting and diarrhea. The coal ash is selected as an adsorbent because it is waste material, which obtained easily and abundantly after coal combustion processes. The adsorption of xylenol orange was performed at different pH. The obtained adsorption data was also fitted to Langmuir adsorption isotherm and then calculated the corresponding adsorption parameters.

EXPERIMENTAL SECTION

Materials

xylenol orange was purchased from Merck chemical company. The coal sample was collected through PMDC (Pakistan Mineral Development Corporation) according to the standard methods of sample collection from Harnoi (Abbottabad) coal mine. ROM (Run of Mine) coal sample was obtained in the form of lumps, which was ground using grinder.

Preparation of coal ash

The crushed coal sample was heated in muffler furnace at 750°C until the whole carbonaceous materials were removed. The coal ash was then screened through a screener (60 μm mesh size) and stored for further use.

Adsorption Kinetic and equilibrium isotherm onto coal ash samples

One gram coal sample and 30 ppm xylenol orange solution (50 mL) was stirred at room temperature for different time duration separately, and determined the equilibrium time. The equilibrium isotherm was also studied as a function of xylenol orange concentration at equilibrium time. The concentration of xylenol orange in solution was determined by spectronic-20 spectrophotometer. The adsorbed concentration (mg/g) of xylenol orange was calculated as follows:

$$q\left(\mathrm{mg/g}\right)=\frac{\left(C_0-C_f\right)V}{M} \tag{1}$$

where q is the amount adsorbed (mg/g), C_0 is the initial Tartrazine concentration, C_f is the final Tartrazine concentration (mg/L), V is the solution volume (L) and M is the amount of adsorbent used (g) [15].

RESULTS AND DISCUSSION

Fig. 1 shows the EDX analyses of coal ash, which presented the wt % of different elements in the adsorbent. The coal ash showed highest wt % of silicon (26.8 wt %), aluminum (8 wt %), iron (7 wt %), magnesium (0.94 wt %) and titanium (0.88 wt %) while other elements are present in minute quantities.

Kinetic study for the adsorption of xylenol orange onto coal ash

For the sufficient removal/recovery of the dyes from different sources, the adsorption time should be short enough for the time consuming in the experiments in the laboratories and for the industrial applications. In this study the coal ash, which was obtain after coal combustion was used as an adsorbent for the removal/adsorption of xylenol orange from aqueous solution. The adsorption of xylenol orange onto coal ash at different time duration is shown in Fig. 2. The kinetic study was carried out at room temperature. Fig. 2 shows the adsorption capacity of the dye molecules which was increased as increased the adsorption time and then almost constant after 40 min. It was also found that the coal ash removed about 80 % of dye from the aqueous solution within 40 min. It is found that the rate of xylenol orange adsorption was rapid, initially and then slow down gradually until it attained the equilibrium and beyond that there was no significant increase of dye adsorption. This might be due to the saturation of active surface sites of the adsorbents.

Statistically, the relation between the adsorption of xylenol orange onto coal ash and different adsorption time was calculated by using Spearman rank correlation coefficient, which is given below.

$$r_s=1-\frac{6\sum d^z}{m^3-n} \tag{2}$$

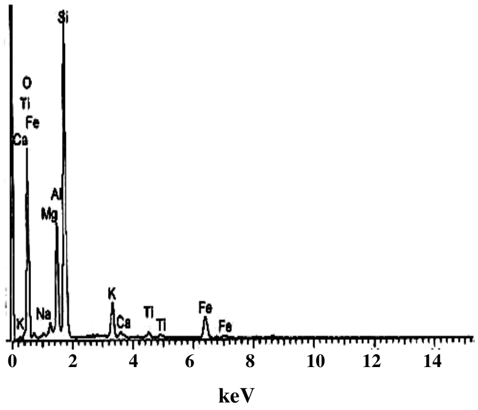

Fig. 1: EDX study of coal ash.

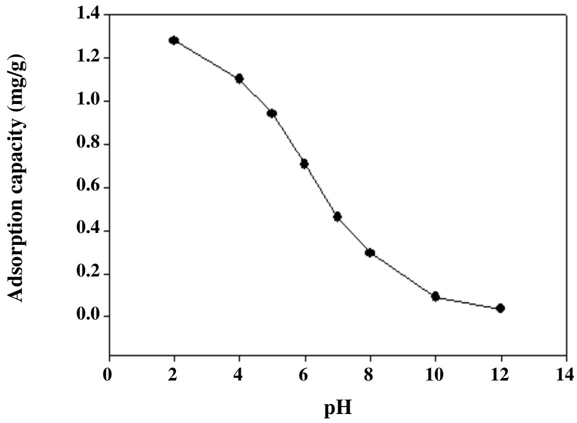

Fig. 3: Adsorption of xylenol orange onto Coal ash at different pH.

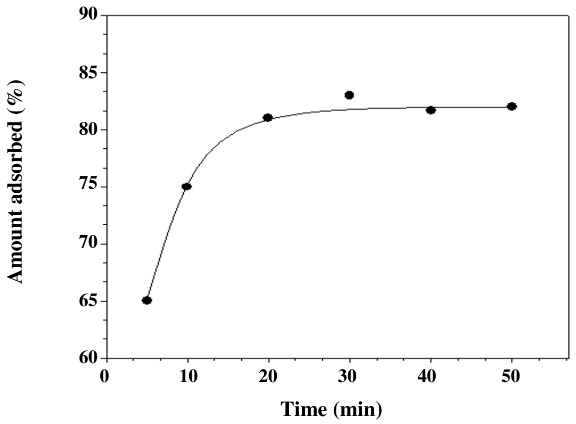

Fig. 2: Adsorption of xylenol orange from aqueous solution on coal ash, as a function of time.

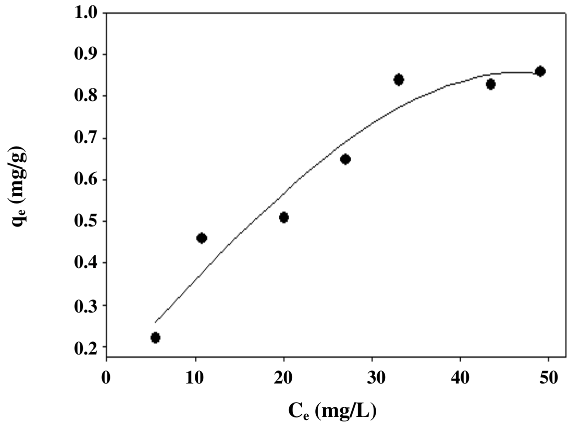

Fig. 4: Adsorption isotherms of xylenol orange onto coal ash.

$$r_s = 0.82 \qquad (3)$$

Where r_s represent the correlation coefficient, d represent the difference between the ranks of observations and *n* shows the number of observations. The coefficient of correlation shows that there is strong positive correlation between time and xylenol orange adsorption. It shows that the dye adsorption and adsorption time depend 82.3 percent on each other.

The adsorption of xylenol orange was also carried out at different pH 2, 4, 6, 7, 8, 10 and 12 at room temperature. Fig. 3 shows the effect of pH on the adsorption of xylenol orange on coal ash. The coal ash adsorbed high quantity of xylenol orange at low (acidic) pH 2. The adsorption of the dye was decreased as further increased in pH. It is reported that in aqueous solution, acidic dye is first dissolve and then dissociate and as a result anionic dye ions are formed [2]. It is also reported [16], that at low pH, positive charge sites created on the adsorbent surface in contact with water. It result a significantly high electrostatic attraction between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increased, the number of negatively charged sites increased and the number of positively charged sites decreased. A negatively charged surface site on the adsorbent did not favor the adsorption of dye anions due to electrostatic repulsion.

Adsorption Isotherm

Fig. 4 shows the equilibrium adsorption isotherm studies of xylenol orange on coal ash. The equilibrium adsorption isotherm studies were performed at 40 min using various equilibrium concentrations at room temperature. The results in Fig. 4 indicate that initially the adsorption of xylenol orange onto the coal ash was increased as increased in the concentration of

Table 1: Langmuir and Freundlich constants for xylenol orange adsorbed on coal Ash.

Langmuir Model		Freundlich Model	
q_m	K_L	N	K_f
0.74	19.78	0.60	1.05

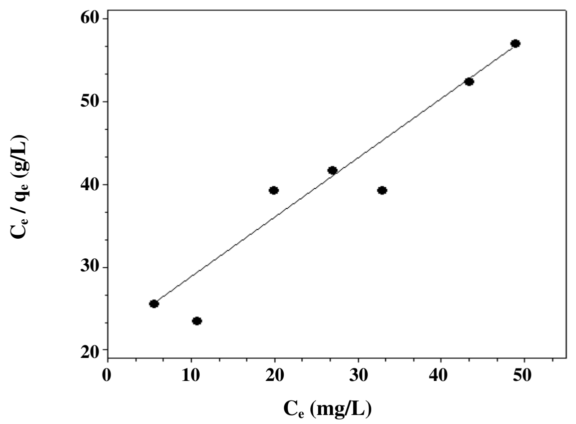

Fig. 5: Langmuir isotherms of Tartrazine xylenol orange onto coal ash.

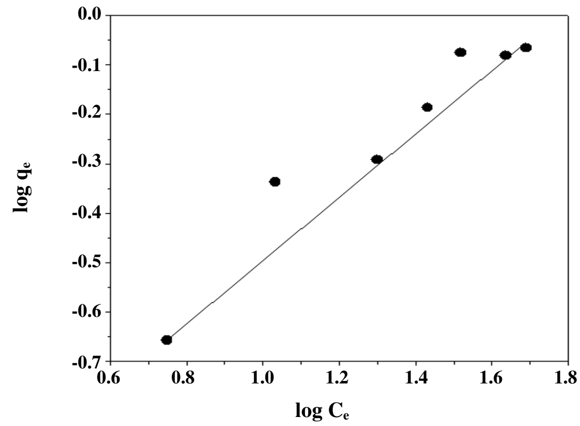

Fig. 6: Freundlich adsorption isotherm of xylenol orange onto coal ash.

adsorbent and then almost constant after using certain concentration. The initial increase in the adsorption of xylenol orange might be due to the availability of many active sites on the coal ash surface and then the adsorption equilibrium was reached to maximum due to the surface saturation of the adsorbent [17].

The statistical association between the different concentration of dye and its adsorption at equilibrium time was calculated by Spearman rank correlation coefficient (Eq. (2)). The correlation coefficient shows that there is a strong positive relation (r = 0.98) between different concentration and removed pollutant. The trend line shows that the amount of the dye removal from aqueous solution increases with the increase of concentration.

The equilibrium adsorption data were also fitted to Langmuir and Frandlich adsorption isotherm models, in order to study weather adsorption occur separately in mono layers or multi layers or both mono as well as multi layers on coal ash adsorbent.

The Longmuir adsorption isotherm was calculated by the following equation [18].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{4}$$

Where q_m is the amount of xylenol orange adsorbed on coal ash samples (mg/g), C_e is the equilibrium concentration (mg/L), and q_m and K_L are the Langmuir constants related to adsorption capacity and binding energy, respectively. Table 2 shows the values of q_m and K_L, which were calculated from the slope and intercepts of the plot (Fig. 5).

The Langmuir adsorption isotherm presents that the adsorption/sorption occurs in monolayer. It means that once the active site on the adsorbent is occupied by the adsorbate then further no adsorption occurred at that active site (saturation reached beyond which no adsorption take place) [15].

The equilibrium adsorption data is also fitted to Freundlich model. The Freundlich model is not limited to monolayer adsorption but shows adsorption in multilayer. The Freundlich model is the most important multi-site adsorption isotherm for heterogeneous surfaces [19]. The logmeratic form of the Freundlich model is shown by the following equation:

$$\log q_m = \log K_f + 1/n \log C_e \tag{5}$$

Where q_m are the quantity of xylenol orange adsorbed on adsorbent (mg/g), C_e is the equilibrium concentration (mg/L). While K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When log q_e was plotted vs. logC_e, a straight line was obtained with slope 1/n (Fig. 6). The results indicated that the adsorption of xylenol orange onto coal ash samples also follow Freundlich adsorption isotherm [20]. The values of K_f and n are presented in Table 2.

CONCLUSIONS

The coal ash obtained after the coal combustion, is efficiently removed of xylenol orange from the aqueous solutions. The adsorption of the dye molecules onto the coal ash increased till 40 minutes of equilibrium time. It was also found that the high concentration of xylenol orange was removed at low pH. The equilibrium adsorption data (obtained after different dye concentration) was also followed both the Langmuir and Freundlich adsorption isotherms.

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