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Preparation of Activated Carbon from Coal by Thermo-Chemical Methods and Its Application on Industrial Effluent for COD Reduction

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Abstract. This study was conducted to assess reduction of chemical oxygen demand (COD) of textile industrial effluent by activated carbons prepared from locally available coal. Activated carbons were prepared by thermal activation at 700 °C and chemical activation with phosphoric acid (H_3PO_4) at the same temperature. The complete study was carried out in batch adsorption mode to investigate the effect of operating parameters. The results of COD reduction with thermally activated carbon (TAC) and chemically activated carbon (CAC) compared and optimum operating conditions were determined for maximum reduction. Freundlich adsorption isotherm was applied besides the calculation of optimum treatment parameters for maximum reduction of COD concentration from effluent of the textile industrial plant. The percent yield of TAC and CAC was 69% and 82%, respectively and maximum percentage reduction of COD concentration under optimum operating conditions using TAC and CAC was 86.9% and 95.9%, respectively.

Keywords: activated carbon, coal, textile wastewater, isotherm, COD

Introduction

In the last few decades, rapid population and industrialization increase have changed the state of different ecosystems on which human beings depends. Untreated waste water of municipal and industrial area is discharged into rivers and oceans and it affects the quality of water and creates pollution. These wastewater effluents hold huge amount of organic pollutants which effects the ecosystem badly, either in biochemical oxygen demand (BOD), chemical oxygen demand (COD) or total suspended solids (TSS), possibly in the tens of thousands mg/L (Ng, 2006).

In the recent years, the correlation among environmental pollution and industrial action had been mostly recorded (Robinet and Feunteun, 2002). In the industrial sector, the paper and textile industries are of particular importance because they produce considerable amount of wastewater effluents that have a very harmful affect when discharged into the natural environment without treatment. The environmental difficulties related to textile sector are induced chiefly by the large utilization of organic dyes (Peralta-Zamora *et al.,* 2003).

When the activated carbon is in contact with an aqueous solution, an electric charge is generated. This charge resulted from either the dissociation of the surface functional groups of the carbon or the adsorption of ions from the solution, and depends on the pH of the solution and on the surface characteristics of the adsorbent (Li *et al.,* 2002). The crystalline structure, surface edges, porosity, variable characteristics of surface chemistry, and high degree of surface reactivity in activated carbon (AC) regulate the adsorption efficiency (Malik *et al.,* 2004). Activated carbon is commonly used as an adsorbent in sugar refining, chemical and pharmaceutical industrial water and wastewater treatment (Ng *et al*., 2003).

Chemical activation (ChA) is a one-step method used for the preparation of AC. Different chemical activating agents (H_3PO_4, KOH, H_2SO_4 etc.) might be used (Macia-Agullo *et al*., 2004). Major advantages of ChA are the higher yield, lower temperature of activation (less energy costs), less activation time and, generally, higher development of porosity; among the disadvantages are the activating agents costs and the need to perform an additional washing stage to remove the chemical agent.

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In the present study chemical oxygen demand (COD) parameter for analysis of pre and post treated wastewater was focused. The objectives of the research work were to prepare activated carbon from indigenously available coal for the reduction of COD, investigating various optimum conditions for activated carbon efficiency and application of the prepared activated carbon in treating industrial wastewater and comparison of different application methods.

Materials and Methods

Sample collection. Wastewater samples from Nishat Textile Industry (located at Hudiara drain, Lahore) were collected by grab sampling technique (Kaul and Gautam, 2002), then these sample aliquots were mixed to form a composite sample and preserved in refrigerator. Samples after collection were analyzed for both physical and chemical parameters (Table 1) but only COD parameter was focused.

Table 1. Laboratory analysis of wastewater samples along with National Environmental Quality Standards of Pakistan (NEQS, 2000)

Parameters	Wastewater characterization	NEQS (2000) (mg/L)
Colour	Brownish black	---
Odour	Irritating	---
pH	5.5	6 - 9
Temperature (°C)	31	$\leq$ 3 °C
Total solids (mg/L)	7480	3700
Total dissolved solids (mg/L)	5720	3500
Total suspended solids (mg/L)	1760	200
Chemical oxygen demand (mg/L)	1450	150
Sulphide contents (mg/L)	8.928	1
Chloride contents (mg/L)	378	1000
Total organic carbon (%)	0.0279	---

NEQS = National Environmental Quality Standards.

Activated carbon preparation. Indigenously available coal of *Acacia nilotica* wood was purchased from wood stall and used for the preparation of activated carbon. The coal obtained from wood stall was not only easily available but was least expensive Activated carbon was synthesized from coal by thermal and chemical activation. For TAC, coal was first washed, dried at 110 °C then burnt in a furnace at 700° C for 3 h to convert it from simple carbon to activated carbon having adsorption sites. For CAC, phosphoric acid was selected because it was an efficient activating agent for synthetic activated carbon with high surface area and pore structure (Attia *et al.,* 2008). Coal was ground, washed, dried and treated with phosphoric acid at the ratio of 35 mL/250 g of coal for 24 h (Gueu *et al.,* 2007). After treatment this carbon was activated in a furnace at 700 °C for 3 h.

Batch adsorption experiment. To reduce the COD of wastewater by activated carbon, batch adsorption study was carried out at room temperature 25±3 °C. For experiment 100 mL of wastewater sample was taken in a 250 mL conical flask and treated with different weight (1 to 10 g) of AC at different pH (2 to 12) and contact time (1 to 5 h). Glass beads were used in the conical flask to ensure complete contact between activated carbon and solution.

Chemical oxygen demand (COD) measurement. Measurement of COD was carried out by APHA standard methods (2005) in which 20 mL of sample was mixed with 0.1 g of mercuric sulphate and 2 mL of sulphuric acid reagent followed by addition of 10 mL potassium dichromate, then it was again mixed with 28 mL of sulphuric acid reagent. Then, it was placed under condenser and evaporated and condensed for two hours, removed and cooled down added 3 to 4 drops of Ferroin indicator. After complete mixing, it was titrated against ferrous ammonium sulphate; first the colour was faded, then brick red end point appeared. COD of pre and post treated samples were measured and percentage reduction in COD was calculated as follows:

$$\% \text{ Reduction in COD} = \frac{(X - Y) \times 100}{X}$$

X = the initial COD (mg/L) of wastewater
Y = the COD (mg/L) of filtrate

Freundlich isotherm. Freundlich equation can be written as:

$$x/m = k\, Ce^{1/n}$$

Where:

x/m = qe (mg/g) is the amount of COD removed (x) per unit mass of adsorbent (m); Ce (mg/L) is the residual COD concentration of aqueous solution; k and 1/n are Freundlich constants and measure of adsorption capacity and adsorption intensity, respectively, which can be calculated graphically.

Results and Discussion

In the present work, activated carbon was prepared by physical (TAC) and chemical (CAC) activation methods.

Suhas *et al.* (2007) also reported physical and chemical methods for the preparation of activated carbon.

Activated carbon prepared was observed to be efficient in reduction of COD from industrial wastewater i.e. 87% and 96% with TAC and CAC, respectively at treatment time of 4 h. This result matched with Devi and Dahiya (2008) who observed that percentage reduction of COD with mixed adsorbent carbon was 93.84% after treatment time of 150 min, whereas maximum reduction with commercial activated carbon was 94% after a treatment time of 180 min.

Yield of activated carbon. The yield of thermally activated carbon was found to be 69% while that of phosphoric acid activated carbon gave yield of 82%. The rest was lost during washing and activation process (Table 2). This is in accordance with the yield calculated by Alcaniz-Monge and Illan-Gomez (2008) from physical and chemical activation of coal as 68% and 89%, respectively. One of the important advantages of the chemical process over the physical process was that the yield tends to be greater as carbon burnt to ash was negligible in chemical process.

Table 2. Characteristics of prepared TAC and CAC and their optimum conditions

Characteristics	TAC	CAC
Yield (%)	69	82
Particle size (mm)	0.25	0.25
Moisture content (%)	9.1	8.3
Surface area (m^2/g)	710	730
Bulk density (kg/m^3)	145	157
Porosity (%)	83	87
Optimum pH	2	4
Optimum contact time (h)	4	4
Optimum adsorbent dose (g/100 mL)	8	7
Optimum agitation speed (rpm)	600	500

TAC = thermally activated carbon; CAC = chemically activated carbon.

Mode of study. The study was carried out in Batch adsorption mode. Kadirvelu *et al.* (2003) has also carried out the similar kind of work in batch adsorption mode. Attia *et al.* (2008) used both batch adsorption and column adsorption study for the adsorption of dye using activated carbon impregnated with 70% phosphoric acid and carbonized at 700 °C reveal the best properties which prevailed upon raising concentration of the treated dye to150 and 200 mg/L.

Effect of pH on adsorption efficiency. From the results, it was evident that COD reduction was increased from neutral to acidic pH. It was assessed that maximum values were obtained at pH 2 and pH 4 with TAC and CAC, respectively (Fig. 1 and 2) because at low pH the positively charged species start to dominate and the surface tends to posses positive charge, while the species that are adsorbed were still negatively charged. Due to positively charged adsorbent surface, the increasing electrostatic attraction between positively charged adsorbent particles and negatively charged adsorbate species would lead to boost adsorption of reactive dye (Shukla *et al.,* 2002). Higher adsorption rate of fluoride at low pH was achieved by Karthikeyan and Illago (2007) in which they showed that the surface charges of the adsorbent play an important role.

Yi *et al.* (2008) observed that the initial pH increasing from 3 to 7, the COD reduction efficiency of dye after 60 min of electrolysis increased accordingly. Reddy and Kotaiah (2006) also observed that equilibrium sorption capacity of the activated carbon decreased with the increase in pH values of reactive dye solution, while increase in adsorption towards basic pH (8 to12) with TAC and CAC (Fig. 1 and 2) may be due to increase in OH^- ions as a result of coagulation of pollutants, and thus, are adsorbed. Malik *et al.* (2004) observed similar findings, that in alkaline medium, the extent of dye colour removal increase as pH increased from 8 to 9.

Effect of contact time. Adsorption increased with increase in contact time because there was much time for pollutants to adsorb on the surface of activated carbon. Initially the percent reduction efficiency of CAC and commercial activated carbon was almost similar but at 4 h contact time CAC had adsorption efficiency (95.1%) higher than commercial activated carbon (93%) but the percent reduction in COD of both these were higher than TAC at pH 2 (Fig. 3). Wang *et al*. (2008) showed similar observation that the degree of colouration and total organic carbon of the dye solution decreased significantly with an increase in the contact time until equilibrium was attained.

Effect of activated carbon dosage. It was observed that adsorption capacity increased with increased amount of activated carbon due to increased surface area, as more sites were available for adsorption. In case of thermally activated carbon maximum reduction of COD was observed at 8 g and after that it became constant while in case of chemically activated carbon reduction became maximum at 7 g (Table 2).

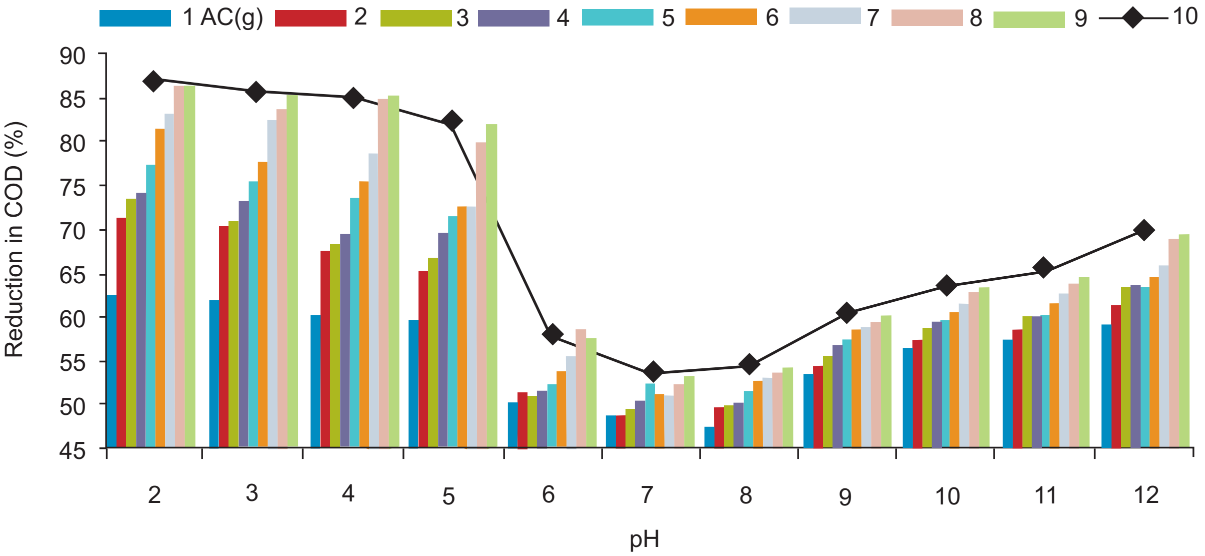

Fig. 1. Effect of pH and adsorbent dose on percent removal of COD with TAC.

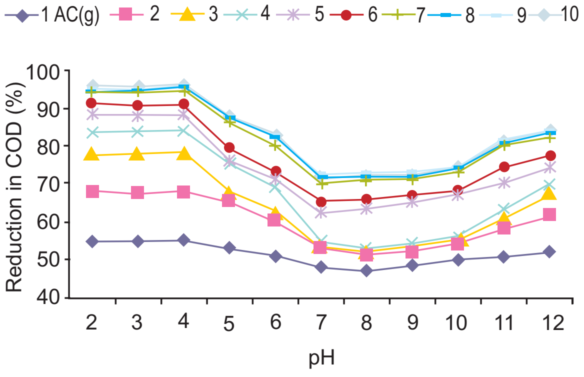

Fig. 2. Effect of pH and adsorbent dose on percent removal of COD with CAC.

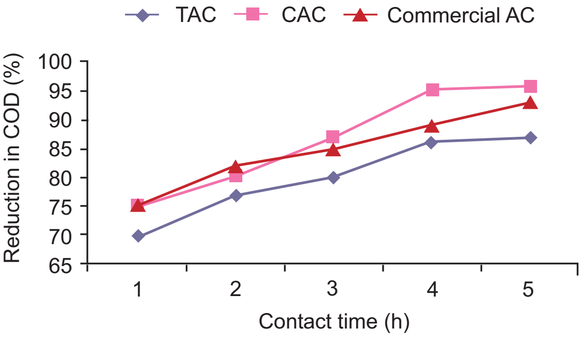

Fig. 3. Effect of contact time on percent removal of COD with TAC, CAC and commercial activated carbon.

It was observed It was also observed that adsorption capacity of CAC was more than that of TAC due to the formation of more adsorption sites by chemically activated carbon (Fig. 4 and 5), that was also observed by Reddy and Kotaiah (2006) that by increasing the dose of commercial activated carbon and sludge derived activated carbon, the percent removal of dye from aqueous solution increased.

Namasivayam and Kavita (2002) were of the view that increase in the adsorption capacity of the adsorbent material with increased dosage indicated the availability of abundance of active sites on its surface. Singh *et al.* (2008) showed that, initially the percentage removal increases very sharply with the increase in adsorbent dosage (1-5 g/L) but beyond a certain value, the percentage removal reached almost at constant value.

Effect of agitation speed. Agitation speed directly effected the reduction in COD of industrial wastewater. The results showed that adsorption increased with both TAC and CAC by increasing agitation speed and reduction in COD was maximum at 600 and 500 rpm, respectively (Table 2). Devi and Dahiya (2008) observed maximum reduction in COD at 600 rpm with mixed adsorbent carbon and commercially available activated carbon. Characteristics of activated carbon are shown in Table 2 which closely resemble with findings of Devi *et al.* (2008).

Comparison of TAC, CAC and commercial activated carbon. Reduction efficiency of COD with TAC, CAC and commercial activated carbon was compared at pH 2 and 4 as TAC adsorbed efficiently at pH 2 than at pH 4 while CAC adsorbed maximum at pH 4. Adsorption of commercial activated carbon was lower than both TAC and CAC at pH 2 but it was higher than TAC at pH 4 (Fig. 4 and 5). Initially at pH 2 the adsorption efficiency of TAC was more than that of CAC but with the increase in carbon dosage this difference became minimized, and at 8-10 g of activated carbon it became constant with both (TAC & CAC) adsorbents (Fig. 4). At pH 4 adsorption efficiency of TAC and commercial activated carbon was more than CAC in the start (from 1-2 g of adsorbent dose) but at adsorbent dose of 3 to 10 g, CAC showed more adsorption efficiency than TAC and commercial activated carbon.

Adsorption isotherm studies. Freundlich isotherm is the earliest known relationship describing the sorption equation. This farely satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogenous surface energy system (Lee *et al.,* 1995). The Freundlich isotherm corresponding to the experimental measurements for TAC and CAC were plotted on log scale as shown in Fig. 6 and 7, respectively. Values of regression coefficient (R^2) had been calculated from the linear fit and are based on the fit, the respective values of the slope 1/n and intersect on y-axis taken as k was also calculated. Values 1/n, k and regression coefficient R^2 for TAC and CAC are shown in Table 3, corresponding to COD concentration reduction.

As value of R^2 was closer to 1, it showed the fittest of the result of this study in Freundlich isotherm. From the Table 3 it is observed that the data fitted well in Freundlich isotherm with high correlation coefficients (R^2) value of 0.9587and 0.9045 for CAC and TAC, respectively. This high correlation coefficient confirms the applicability of the isotherm. Amuda and Ibrahim (2006) reported that the constants 1/n and k were of definite importance in determining

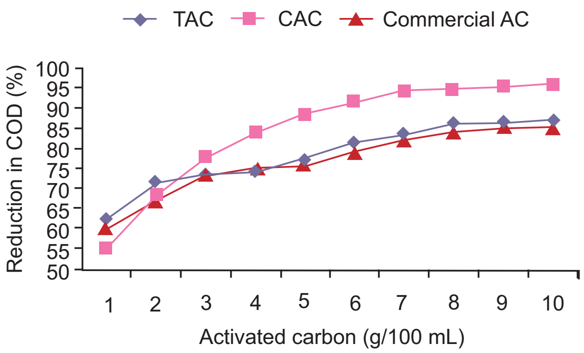

Fig. 4. Comparison of TAC, CAC and commercial AC at pH 2 and 4 h contact time.

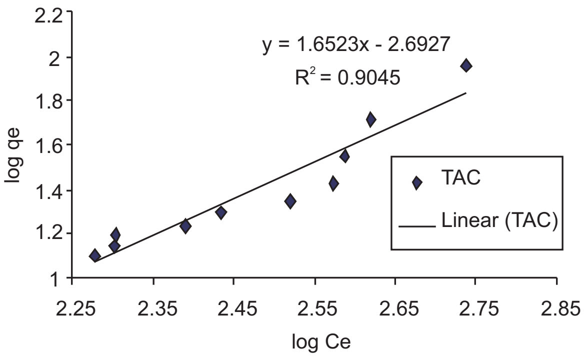

Fig. 6. Freundlich isotherm study of TAC at optimum pH and contact time.

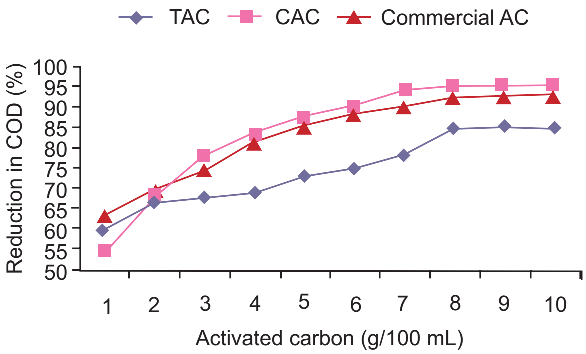

Fig. 5. Comparison of TAC, CAC and commercial AC at pH 4 and 4h contact time.

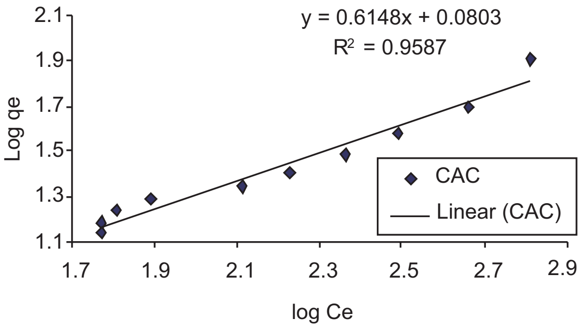

Fig. 7. Freundlich isotherm study of CAC at optimum pH and contact time.

the adsorption capacity of organic pollutants from wastewater and reduction of COD concentration by adsorbents. The slope 1/n was dependent on the order of the change in reduction of COD concentration with the adsorbent dose, while k was dependent on extent of reduction of COD by the adsorbents. Table 3 shows high value (2.936) of k indicating good adsorption efficiency of CAC, while higher value of 1/n indicates more change in effectiveness over different equilibrium concentrations.

Table 3. Freundlich isotherm constants for COD adsorption.

Activated carbon	k	1/n	Regression coefficient (R^2)
TAC	0.0246	2.6927	0.9045
CAC	2.936	0.0803	0.9587

TAC = thermally activated carbon; CAC = chemically activated carbon.

Conclusion

Present study showed that both activated carbons (TAC and CAC) are effective for reduction of COD concentration from effluent of textile industry. Adsorption of COD was found to be dependent on pH, treatment time and adsorbent dose. The studied adsorption data fitted well to Freundlich adsorption isotherms. This adsorbent prepared from coal could be a good alternative to expensive activated carbon and hence wastewater treatment process can become very economical. A certain amount of work has already been done on the production of ACs from coal, as well as on the adsorption of inorganic and organic pollutants on coal and coal-derived activated carbons (ACs), there is still a need for more detailed systematic studies.

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