
Abdolmajid Gholizadeh 1, Mitra Gholami 2, Ali Asghar Ebrahimi 1, Mohammad Miri 1*, Ali Nikoonahad 1

1 Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.
2 Department of Environmental Health, School of Public Health, Iran University of Medical Sciences, Tehran, Iran.

ABSTRACT

Introduction: The Powdered Activated Carbon Treatment (PACT) has been proposed as an alternative in wastewater treatment and wastewater biomass protection against toxic substances. This study aims to evaluate PACT performance in treating dyes, acid orange, and remazol brilliant reactive blue.

Materials and Methods: This empirical-applied research was carried out in pilot scale in which different dye removal systems were tested: activated sludge, PAC, and the combined activated carbon–biomass system. The degradability of selected dyes was evaluated through Zahn-Wellens method. Also, tests continued by adding different concentrations of powdered activated carbon and its effect on activated sludge in different operating conditions was investigated. American Dye Manufacture Institute (ADMI) method was utilized for determination of dye removal in samples.

Results: Results revealed that dye removal in combined carbon–biomass system was faster and more efficient than activated sludge individually. So, in the wastewater with the dye concentration of 100 ppm, the dye removals through biological process alone were equal to 60 % and 12.5 % for acidic and reactive dyes, respectively. The best PAC efficiency in activated sludge process was obtained in 1500 mg/L PAC concentration. Hydraulic Retention Time (HRT) and the optimum temperature of dyes’ removal were determined 28 hours and 30 °C, orderly; in these conditions the dye removal efficiency of 98.18 % was obtained. Also the dye removal using activated carbon–biomass system was adequately described by combining the kinetic equations.

Conclusion: PACT could be considered as an acceptable and highly efficient method for removal of different dyes in textile industry.

Introduction

The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals. About 15 % of the total world’s production of dyes is lost during textile dyeing, which is released in textile effluents 1, 2. Currently, more than 10,000 various types of dyes are synthesized and available worldwide. Although no recent data is available on global dye production, annual production of over 700,000 tones has been often reported in the literature 3, 5.

Synthetic dyes are widely used for dyeing and printing in a variety of industries. Large volumes of colored aqueous effluents are discharged into the environment by various sectors, such as textiles, leather, printing, laundry, tannery, rubber, plastic, painting, and other industries 3, 6, 7. The
existence of very low concentrations of these dyes is highly visible and undesirable that can potentially inhibit photosynthesis. These industrial effluents are characterized by high chemical oxygen demands (COD) biological oxygen demands (BOD), suspended solids, and intense color. Releasing of Textile effluents to water bodies has raised much concern due to the potential of health hazards associated with the entry of toxic components into the food chains of humans and animals. Since the dyes are stable to light, heat, and oxidizing agents as well as resistant to aerobic digestion, it is difficult to remove them from effluents. Even the presence of very low concentrations of dyes (less than 1 mg/L) in the effluent is considered undesirable which needs to be removed before the wastewater can be discharged into the environment.

Many investigations have reported various methods for removal of dyes from water and wastewater, including biological processes, combined chemical and biochemical processes, chemical oxidation, adsorption, coagulation, and membrane treatments; each of these has specific advantages and disadvantages.

Among the various chemical and physical methods, adsorption seems to be a comparatively efficient. A wide range of sorbents have been examined for the removal of phenol from aqueous solutions, among which activated carbon is accepted as the most powerful and thus extensively used adsorbent. The adsorptive properties of activated carbons result from their high surface area and high degree of surface reactivity. Activated sludge (AS) treatment is a technically and economically feasible option to treat many types of wastewaters containing highly biodegradable organic matters. In a study conducted by Rezaei Kalantry R. et al. the magnetic-activated carbon (MAC) was synthesized and employed as an adsorbent for removing Reactive Blue 5 from aquatic environments. They concluded that the adsorbent is very suitable for dye removal from aquatic media due to its high efficiency, quick and easy isolation and also because it does not lead to the secondary pollution. Also, in another study carried out by Gholizadeh et al., a porous adsorbent was produced and tested for the removal of phenolic compounds (phenol, 2-chlorophenol and 4-chlorophenol). Results indicated that the synthesized powder could effectively remove high concentrations of external pollution in a short contact time.

Refractory organic compounds and heavy metals often have negative effects on micro-organisms in activated sludge. However, adding powdered activated carbon to aeration tank (PACT process) can remove refractory, toxic, and/or inhibitory organic compounds, and also is able to enhance nitrification and sludge dewater ability. Thus, the powdered activated carbon treatment system can remove organic compounds more efficiently than either biodegradation or adsorption alone.

The dyes used in the present study, i.e., Remazol Brilliant Blue and Acid Orang were chosen from the most important dyes in textile industry. They are frequently used as the starting material in polymeric dyes production and are represented as an important class of toxic and recalcitrant organo pollutants. Therefore, the objectives of this study were (a) to determine the effect of temperature on dye removal efficiency and (b) to analyze the effect of different PAC concentrations on the growth kinetics of activated sludge.

Materials and Methods

**Biological and chemical materials**

In order to remove dyes from waste in textile industry, Powdered Activated Carbon was chosen. Then, to determine the effectiveness of this combination - powdered activated carbon with a density of 0.495 g/m³, ash content of 4 %, moisture of 2.8 %, and active surface of 540 m²/g were purchased (Made in Iran).

Synthetic wastewater contained Carboxymethyl cellulose, ammonium chloride, potassium phosphate, calcium chloride, magnesium sulfate, chloride trivalent iron, zinc, and potassium bicarbonate. Used dyes including acid orange 7 C.115510 and Remazol Brilliant blue were purchased from Fluka Company and their characteristics are as follows (Table 1):
Table 1: Properties of used dyes

<table>
<thead>
<tr>
<th>Properties</th>
<th>Remazol Brilliant blue</th>
<th>Acid orange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3}</td>
<td>C_{16}H_{11}N_{2}NaO_{4}S</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>626.53</td>
<td>350.32</td>
</tr>
</tbody>
</table>

Pilot design

The used pilot had two parts, including an aeration tank (volume of 40 liter) and a settling tank (volume of 12 liter) made from Plexiglas (see its schematic in figure 1).

A separate tank with a volume of 30 liters was considered for mixing powdered activated carbon in water, mixing was performed by a sub-air pipe activated in the required time. The required amount of carbon powder was injected into aeration unit through a dosing pump in specified flow rates.

Wastewater was injected from a raw sewage tank to the aeration unit through a dosing pump and the required air was supplied by a compressor. To generate uniform and subsequent air bubbles and have a uniform mixture, two fine bubble-diffusers were installed in parallel on the floor of aeration unit. Cylindrical clarifier and sedimentation hopper made from Plexiglas were designed and constructed. The useful volume of this clarifier was 12 liters which included a cylindrical part (7 liters) and a terminal cone (5 liters).

After liquid removal from the aeration unit, the mixed liquid gently entered from the center of clarifier to the hopper gravitationally so that it would not create turbulence. An outlet overflow with an adjustable height was considered. Proper slope of the terminal cone collected sludge by gravity and then the collected sludge was returned to the aeration unit by airlift pump. Schema of the applied pilot is portrayed below:

Figure 1: The schematic of the applied pilot
Analytical methods
Since the methodology applied in this research was based on the experimental data, this study is considered as a fundamental – applied research. The statistical method used to determine the number of samples was Box-Benken method which was applied through the Design Expert software (version 7.0.1). Based on the independent and dependent variables and given that the coefficient α = 0.05, number of samples required for multivariate statistical analysis (pressure, temperature, pH, and concentration) was equal to 30. Each test was triplicate in each run and also the statistical tests of regression and correlation were employed. The statistical reliability of the data obtained from the pilot in each step was determined using the SPSS software (version 18).

Growth substrate removal experiments on biomass in the absence of PAC
In the initial step, in a period of thirty days, microbial mass was adapted with wastewater built of Carboxymethyl cellulose as COD generator (500 mg/L of soluble COD) using aeration discontinuous and activated sludge system with returning rate of 100 % to municipal sewage treatment. Then, the concentrations of 0.01, 0.05, 0.1 and 1 mg/L of acidic and reactive dyes were gradually added to this adapted environment. Daily rate changes of SCOD and Mixed Liquid Suspended Solids (MLSS) were also measured. The microbial biomass along with the wastewater as raw seed were transferred to the pilot system only after seven consecutive days through which no significant statistical difference was observed between the test results (SCOD concentration output), with a confidence interval of 95 % (P < 0.05). After stable conditions were established in the operating system, the degradation rate of wastewater containing dyes was studied with different concentrations mentioned above by Zahn-Wellens method (ISO 9888) 24. So, degradation of organic compounds dissolved in water or wastewater was studied during the period of 28 days using aerobic microorganisms. During the test, COD, color, biomass concentration, pH, temperature, and dissolved oxygen concentrations' parameters were analyzed. Dye concentrations determined the basis of color unit, ADMI 25.

The turbidity of the samples was determined and they were passed from cellulose nitrate membrane filter (0.45 microns) to prevent overlapping of input and output data. The method of measuring the characteristics of wastewater have been given in Table 2.

The percentage of COD removal at different times is determined using the following formula:

\[
\text{COD removal} \left(\%\right) = \left[ 1 - \frac{P_{cT} - P_{cB}}{P_{cT1} - P_{cB1}} \right] \times 100
\]

Table 2: Methods used for evaluating the wastewater characteristics

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Used measurement method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>ADMI method</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>Open Reflux Method, 5220 B.</td>
</tr>
<tr>
<td>Biochemical oxygen demand</td>
<td>Using from BOD bottle, 5210 B.</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>Filtration and determination of the weight after heating 2540D,E</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>Winkler’s modified Iodometry 4500-5B</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>Sedimentation on standard cylinder</td>
</tr>
<tr>
<td>Sludge volume index</td>
<td>Calculation of suspended and settled solids, 2710-D</td>
</tr>
<tr>
<td>Microorganisms</td>
<td>Direct microscopic observation</td>
</tr>
</tbody>
</table>
Dye removal by combined powdered activated carbon and activated sludge processes

In the next step, powdered activated carbon was added to the system. Through this step, the carbon powder concentration ranged from 500 to 2500 mg/L and was examined by adding a certain amount of Carbon powder and maintaining the wastewater COD and other input parameters constant. Further, the outputs from an acid solution and reactive dyes with a concentration of 100 mg/L (0.01 % Wt) were evaluated.

There after, a wastewater with COD concentration of 500 mg was used. Powdered activated carbon input and other parameters were kept constant; the effect of hydraulic retention time was evaluated in the range of 18 to 30 hours. After determining the optimal amount of powdered activated carbon concentration and hydraulic retention time, the optimum temperature for maximum performance was determined from the range of 22 to 30 °C. At all steps, the samples were taken at specific time intervals and the removal efficiency of ADMI color values were calculated.

Adsorption isotherms

Batch adsorption isotherms were determined using 1-6 (gr/L) concentrations of carbon powder. For this purpose, specific weight of the adsorbent with 100 ml of solution containing different concentrations of dye (50, 100, 150, 200, and 250 mg/L) were placed on shaker at 120 rpm. After specific periods (0.5, 1, 2, 4, 6, and 8 hours) samples were taken and the percentage of dye adsorption was determined. In order to determine the Langmuir and Freundlich adsorption isotherms, experiments were developed at equilibrium time (3 hour) and a constant temperature of 25 °C.

The Langmuir adsorption model that describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface, can be described as the following formula

\[
\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

(2)

Where \(q_e\) and \(C_e\) are the parameters described in Eq. 2, \(q_{\text{max}}\) is the maximum amount of adsorption (mg/g), and \(b\) is the adsorption equilibrium constant (L/mg).\(^{27}\)

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems.\(^{28}\) Freundlich isotherm is calculated by this equation:

\[
q_e = K_F \cdot C_e^{1/n}
\]

(3)

Or in linearized form, Eq. (3) can be written as:

\[
\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)
\]

(4)

Where \(K_F\) is the Freundlich capacity constant (mg/g) and \(1/n\) represents the affinity constant. Moreover, the lower fractional value of \(1/n\) \([0 < (1/n) < 1]\) indicates that weak adsorptive forces are effective on the surface of adsorbent. Then, \(q_e\) and \(C_e\) are the equilibrium dyestuff concentration in solid phase (mg/g) and the equilibrium dyestuff concentration in liquid phase (mg/L), respectively.\(^{13}\)

Results

Growth substrate removal by activated sludge process in the absence of PAC

Obtained results from the first step demonstrated that activated carbon alone did not have sufficient efficiency on removal of acid orange dye and Remazol Brilliant blue dyes from synthetic dye effluents. At the best status, maximum observed removal was equal to 30 % (SD = 2.18), so that the removals of reactive blue dye and acid orange dye were 12.5 % and 60 %, and COD removals were 25 % and 80 %, respectively. These values were very low in comparison with the environmental standards. By considering the influent ADMI equal to 2354 units, the ADMI in effluents were obtained equal to 951.2 and 2211 for reactive and acidic dyes, respectively. Comparison of dye removal in biological processes alone (30 %) with removal rates in combined activated sludge process - powder activated carbon (98 %) indicates that adding powdered activated carbon is able to raise efficiency to about 70 %, especially for reactive dyes (P < 0.01).

Effect of powdered activated carbon concentration

JEHSD, Vol (1), Issue (3), December 2016, 141-52
Figure 2 shows the results of ADMI removal of dye samples with different concentrations of powdered activated carbon in the aeration unit and with 100 mg/L of input dye while the ADMI amount of input was equal to 2710. Results indicated that increasing concentrations of powdered activated carbon from 500 mg/L to 2000 mg/L would reduce the amount of ADMI outputs from 518.46 to 54.31. Also, in powdered activated carbon concentration of 2000 mg/L, the highest dye removal (98.83 %, SD = 0.74) appeared. By taking into account the economic considerations and the fact that dye removal in increasing concentration from 1500 to 2000 mg/L was negligible, the carbon powder concentration of 1500 mg/L was considered as optimum (98.18 % removal).

**Figure 2**: The effect of activated carbon dose on ADMI removal and removal efficiency (The dye concentration of 100 mg/L)

**Effect of hydraulic retention time**
Since the optimum concentration of powder activated carbon to remove dye was obtained as 2,000 ppm from the previous step, at this step, by keeping all variables constant, the effect of changes in hydraulic retention time was evaluated in the range of 18-30 hours on dye removal percentage.

The achieved results represent that by increasing the hydraulic retention time from 18 hours to 24 hours, dye removal increased to 15.8%, and by increasing the retention time to 30
hours, the dye removal rate reached to 98.83%. Thus, changes in retention time have a huge impact on the efficiency of dye removal. For this, the hydraulic retention time of 28 hours was considered appropriate in this study. Figure 3 shows the procedure of ADMI value changes with changing hydraulic retention times:

**Figure 3:** The effect of hydraulic retention times on ADMI and dye removal (The dye concentration of 100 mg/L and PAC = 2000 (mg/L))

**Thermodynamic study**

Temperature of medium affects the removal efficiency of the pollutant from aqueous solution. In the current study, the effect of temperature on the removal efficiency showed that while the effecting parameters of hydraulic retention time and solid volume loading were equal to 30 hours and 20 days, respectively, and the carbon powder concentration of 2,000 ppm was kept constant, temperature changed in the range of 24 °C-30 °C. The results (Figure 4) also showed that increasing temperature from 24°C to 30°C resulted in increasing dye removal rate to 3 %. In other words, at this step, the highest dye removal was observed at 30 °C in which the dye removal and the ADMI in the effluent were 98 % and 54 %, respectively.

**Figure 4:** The effect of various temperatures on ADMI and dye removal

**Adsorption isotherm studies**

Adsorption isotherms were determined for various dye–adsorbent systems. The distribution of dye between adsorbent and the dye solution at equilibrium is important in establishing the adsorbent capacity of the dye.
An equilibrium isotherm expresses the relation between the amounts of adsorbate removed from the solution at equilibrium and adsorbent mass unit at a constant temperature. In the present study, the adsorption isotherms were investigated by applying two equilibrium models, namely the Langmuir and Freundlich isotherm models.

The results of isotherm studies are shown in the Figure 5 and Table 3. Because correlation coefficient ($R^2$) in Langmuir equation (0.99) was greater than Freundlich equation (0.95), it can be concluded that adsorption data follows from Langmuir adsorption model. In the Langmuir equation, $q_{\text{max}}$ is considered the maximum sorption capacity related to the total surface covering which here is equal to 140.85 mg/g and $b$ (here is equal to 5666.4 L/mg) is associated with the sorption energy.

![Figure 5: Langmuir (A) and Freundlich (B) isotherms](image)

**Table 3:** Freundlich and Langmuir equations' constants and coefficients

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>140.85</td>
<td>5666.4</td>
</tr>
</tbody>
</table>

**Discussion**

In this study to investigate the effect of PAC on the bioavailability of growth substrates (acid orange dye and Remazol Brilliant reactive blue dye), adsorption kinetic (hydraulic retention times) was studied. The findings showed that by increasing of contact time, the removal efficiency increased gradually. In addition, after an hour of contact time, the removal efficiency was roughly constant till equilibrium was attained. The higher adsorption rate at the initial period may be due to increasing number of vacant sites on adsorbent in the initial step. As a result, a concentration gradient exists between dye in the solution and dye on the adsorbent surface.

Sarkar et al. studied the reuse of dairy industries’ wastewater using PAC among other procedures. They found that the equilibrium corresponding to adsorption of soluble COD was achieved within the first 2 hours.
Further, batch growth experiments were performed to evaluate the effect of PAC concentration on biomass growth kinetics. For each tested PAC concentration, 1-6 g (PAC/L) and for the experiment without PAC, the observed maximum specific growth rate ($\mu_{obs}$) were calculated from the slope of linear part of Ln (X) plot as a function of time. The investigation showed that activated sludge process alone was not able to remove acid and reactive blue dyes from synthetic wastewater. However, combination of this process with adsorption process could promote the efficiency because of the effect of activated carbon on active bacteria. Moreover, it was found that increasing in powdered activated carbon concentration reduces the amount of ADMI in effluent samples, while in powdered activated carbon with a concentration of 2000 mg/L, the highest percentage of dye removal appeared. In this process, activated carbon suspended in activated sludge provides a platform for dye treating bacteria and therefore the SRT of biomass will be increased. The increasing number of bacteria in wastewater aeration tank causes more use of dyes. Also, as it was entrenched previously, dosage declaration leads to reduction of adsorption ratio because a greater number of active sites will be available on the sorbent. 

Agha mohammadi et al. investigated the effect of activated sludge process for treatment of semi-aerobic landfill leachate with and without adding of powdered activated carbon. Their results showed that enhanced reactor performance was due to PAC addition with higher COD, dye, and ammoniac nitrogen removals. The PAC augmented reactor also had higher concentrations of NO$_2$-N and NO$_3$-N as a consequence of greater degree of nitrification.

Furthermore, the employed statistical test (independent Sample T-Test), represented a significant difference between SCOD concentration and ADMI in the effluent process. Due to absorption of dyes by powdered activated carbon, lower concentrations of initial soluble SCOD were obtained by increasing PAC concentrations. The current results agree with those reported by other authors working on a sequencing batch reactor.

Investigations dealing with the effect of temperature on dye removal showed that increase in temperature would result in dye removal increase. This observation implies that dyes removal in PACT process may be a kinetically controlled process. Raise in temperature leads to an increase in pollutants uptake through the following ways:

1. increasing mobility of dye followed by an increase in the effective interactions between the reacting and the adsorbent material;
2. increasing the pore size of the adsorbent surface. Similar results were also reported by other researchers in the cases of methylene blue dye removal using montmorillonite/CoFe$_2$O$_4$ composite, as well as the removal of Reactive Black 5 dye using magnetic chitosan resins.

Additionally, the Langmuir and Freundlich models were used to describe the resultant adsorption isotherms. The Langmuir isotherm model fitted the equilibrium data better than Freundlich isotherm model, revealing that dyes were absorbed onto the activated carbon through a monolayer adsorption, because the Langmuir adsorption model describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface. Moreover, there is a negligible interaction between the adsorbed molecules and adsorption sites having uniform energies.

**Conclusion**

Abstained results demonstrated that activated carbon alone did not have sufficient efficiency to remove acid orange dye and Remazol Brilliant blue dyes from synthetic dye effluents. So, when the biological process was applied alone to treat the studied dyes, only about 30 % of it was applied, but by adding powdered activated carbon to the activated sludge process, the dyes’ removal efficiency increased about 70 % and rose to 98.8 %. Thus, the activated sludge system enjoys technical feasibility, flexibility, economic benefits, and high efficiency which can be considered as an advanced treatment system without the need for large scale investments. Further, combining the processes of...
activated sludge and powdered activated carbon can be an economical option without requiring any Physico-chemical treatment suitable for dye and COD removal from textile wastewaters.

Acknowledgements
The authors are pleased to express their sincere gratitude to the laboratories at the School of Public Health, Iran University of Medical Sciences and all those who did not withhold their generous assistance to this research.

Funding
The work was unfunded.

Conflict of interest
We have no competing interests.

References
