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# Adsorption of Congo Red onto Bottom Ash

S.M. Saleh, H.I. Maarof, S.N.S.A. Rahim and N. Nasuha
Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM),
Permatang Pauh, Pulau Pinang, Malaysia

**Abstract:** The adsorption of Congo Red (CR) onto Bottom Ash (BA) was studied in batch process. The objective of this study was to compare the adsorption capacity between physical-activated BA and untreated BA for removal of CR. Bottom ash was modified by undergoing pyrolysis process where it was activated in the vertical tubular furnace with the flowing of carbon dioxide at 700°C. Then, the adsorption process was carried out on an orbital shaker at 150 rpm for 24 h. Adsorption equilibrium of CR was attained after 24 h of contact time. The equilibrium adsorption data were interpreted by using Langmuir and Freundlich models. The data shows that physical-activated BA and untreated BA were well described by the Freundlich model. In addition, the amount of CR adsorbed on the adsorbent, $q_e$ was higher using physical-activated BA (106.61 mg $g^{-1}$) as compared to untreated BA (24.36 mg $g^{-1}$). In conclusion, the modification of BA using pyrolysis process offered a significant affects to the performance of the BA for removal of CR.

**Key words:** Adsorption, bottom ash, coal, Congo red

## INTRODUCTION

As the world has industrialized and its population has grown, water became more vital. The effect of this rapid growth is environmental problem with many types of pollution including water pollution. This problem has become government concerns because the effect of the pollution will harm environment and nature life. There are numbers of pollutant those cause water pollution. All pollutants usually come from manufacturing factories such as textile, petroleum, agricultures, municipal and food industries.

Dyeing process is one of the largest contributions to wastewater generation. For instance the uses of dyes are food, printing, cosmetics products and carpets. Among these, textiles industries consume a large amount of water and discharge a large volume of wastewater in order to process textile dyestuffs. There are numerous types of dyes used for multiple applications such as vat, direct, reactive, solvent, sulfur, acid, cationic and disperse dyes (Gupta and Suhas, 2009). Dye is major pollutant that causes water pollution. This is because it may contain toxic, making water are no longer safe for aquatic life and human being. This may also lead to mutation and retarded the growth of humans. Besides that, dyes block the transmission of sunlight throughout the water and then reduce photosynthesis process (De Oliveira Brito *et al*., 2010). These will make aquatic life including aquatic plants difficult to survive and cause them become extinction and loss their habitat.

Various dyes are hard to decolorize due to their chemical structure and synthetic origin (Kang, 2007). Activated carbon is the most prominent adsorbent has been used in decolorizing the dyes in effluent discharging from textiles industries. However, activated carbon remains an expensive material due to higher quality (Hasan *et al*., 2008). Recently, a number of empirical studies focused more to other alternatives which is low cost adsorbent such as biomass fly ash (Pengthamkeerati *et al*., 2010), oil palm ash composite beads (Hasan *et al*., 2008), peat and rice hulls (De Oliveira Brito *et al*., 2010), hazelnut shell (Ferrero, 2007) and sawdust (Mane and Babu, 2011). Bottom Ash (BA) appears as low cost adsorbent because, it is a waste material that produced from combustion of solid fuels. Its disposal is abundant and dumped near the surrounding land which cause environmental problem. Disposal of BA makes authorities concern because it causes the agricultural land barren (Gupta *et al*., 2004). In this study, effect of physical activation of BA was evaluated.

## MATERIALS AND METHODS

**Preparation of activated bottom ash:** Bottom Ash (BA) was obtained from local coal-fired power plant. The BA is a waste material which non-combustible residue of coal

**Corresponding Author:** Hawaiah Imam Maarof, Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Permatang Pauh, Pulau Pinang, Malaysia Tel: +6043823257 Fax: +6043823292

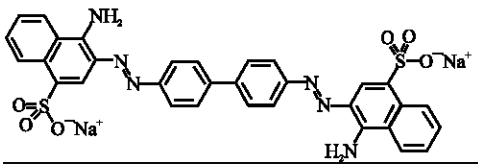
combustion in thermal power plant. It appears as dark gray, granular, porous and sand-like material. Initially, the BA was soaked in deionized (DI) water for 48 h in an open tank without stirring. The DI water then was replaced 2 times for every 24 h. The ratio of BA:DI water used was 1:1.5. On the third day, the BA was filtered and dried in an oven at 105°C for 24 h. Next, it was ground by mortar until the BA was equally fine and was sieved in the size of 500 μm. Then the dried BA undergoes pyrolysis process where it was activated in the vertical tubular furnace with the flowing of carbon dioxide at 700°C for 1 h. After that, it was kept in air-tight container for further use.

**Surface area analysis of bottom ash:** The adsorbents were characterized using accelerated surface area and porosity analyzer (Micromeritics ASAP 2020, USA). The surface area was determined by nitrogen gas adsorption data where Brunauer Emmett Teller (BET) equation was applied as standard method for porous solid characterization. Before performing the gas sorption analysis, the adsorbent was outgassed under vacuum at temperature of 400°C for 4 h to remove any moisture content on the solid surface. The free moisture sample was weighted and the adsorption of nitrogen as a probe species was performed at constant temperature of 77 K. The surface area of adsorbents was calculated based on BET theory. All the calculations and graphs were automatically done and illustrated by the built in software equipped with the Micromeritics ASAP 2020 instrument.

**Preparation of dye solution:** Congo Red (CR) used in this study was of commercial purity. The chemical characteristics of CR are presented in Table 1. The maximum wavelength of CR was analyzed by using spectrophotometer (HACH, DR 2800). Based on the analysis, maximum wavelength of CR was 493 nm. Stock solution of 200 mg $L^{-1}$ of CR was prepared by diluting CR powder with DI water. The experimental solution was obtained by diluting the stock solution to several different initial concentrations ranged between 20 to 140 mg $L^{-1}$.

**Adsorption process:** Adsorption experiment was performed by batch process at room temperature to measure the adsorption characteristic of physical-activated Bottom Ash (BA) and untreated BA with regards to anionic dye. The effect of initial concentration was studied by adding 0.2 g of physical-activated BA in 5 different concentrations of Congo Red (CR) which range between 20 to 140 mg $L^{-1}$. The volume of CR was fixed at 200 mL. The adsorption process was carried out for 24 h and agitated on an orbital shaker at 150 rpm. Then the solutions were left over night to sediment. The remaining

Table 1: Chemical characteristics of Congo red (CR)

| | |
|---|---|
| Generic name | Congo red |
| Chemical name | Disodium 4-amino-3-[[4-[4-[(1-amino-4-sulfonatonaphthalen-2-yl)diazenyl]phenyl]phenyl]diazenyl]naphthalene-1-sulfonate |
| Chemical formula | $C_{32}H_{22}N_6Na_2O_6S_2$ |
| Molecular weight | 696.7 g $mol^{-1}$ |
| Color index number | 22120 |
| Chemical structure |  |

concentrations of CR solutions were measured by using spectrophotometer (HACH, DR 2800). The experiment was repeated using untreated BA with a dosage of 1 g and initial concentration of CR, ranged between 25-125 mg $L^{-1}$.

**Adsorption isotherm:** Adsorption isotherm is useful to describe the interaction between the adsorbent and the adsorbate (solute). It reveals how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The adsorption isotherm data represented by theoretical or empirical equations provides preliminary prediction in modeling steps which is desired to practical operation. In this study, Langmuir and Freundlich isotherms were tested to find the best fit using linear regression coefficient. The linear form of Langmuir isotherm is commonly expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

where, $C_e$ and $q_e$ are defined as the equilibrium liquid-phase concentration (mg $L^{-1}$) and amount of dye adsorbed (mg $g^{-1}$), respectively. Constant b is a direct measure of the intensity of the sorption (L $mg^{-1}$) and it is also related to with energy of the adsorption. $Q_o$ is a constant related to the area occupied by a monolayer of adsorbate which reflecting the maximum adsorption capacity (mg $g^{-1}$).

The Freundlich equation is an adsorption isotherm which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich isotherm is an empirical equation which based on a heterogeneous surface. A linear form of the Freundlich expression is as shown by Eq. 2:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where, $q_e$ is the amount of dye adsorbed per unit mass of adsorbent (mg $g^{-1}$) whereas, $C_e$ is the equilibrium concentration of dye in solution (mg $L^{-1}$). $K_f$ and n are Freundlich constant. $K_f$ represents the quantity of dye adsorbed onto adsorbent for an equilibrium concentration and also can be defined as adsorption of distribution coefficient. Besides that, slope 1/n is a measure of adsorption intensity or surface heterogeneity which indicates that as its value gets closer to zero then it will become more heterogeneous (Hasan *et al*., 2008). The empirical constants $K_f$ and 1/n were determined from the intercept and slope of the linear plots of the experimental data of log $q_e$ versus log $C_e$.

## RESULTS AND DISCUSSION

**Surface area of adsorbents:** Table 2 shows the BET surface area of physical-activated BA and untreated BA. The result indicated that surface area of physical-activated BA is higher than untreated BA. In physical activation, large amount of internal carbon mass is eliminated to obtain a well developed carbon structure. Since porosity of untreated BA has already developed, then during pyrolysis more carbon atoms in the structure exposed to the reaction with carbon dioxide and then more pore widening occurred which caused improvement on the surface area (Ahmadpour and Do, 1996). Meanwhile, Kopac and Toprak (2007) reported that increase surface area of adsorbent in high temperature can be attributed to the release of volatiles components to leave the space that was previously occupied by the decomposed sample and hence contributes to increase in adsorption capacity. In addition, Table 3 lists some other reported findings on BET surface area for various adsorbents. It shows that physical activation of waste material is one of the prominent methods to produce high the surface area of adsorbent.

**Adsorption equilibrium:** Figure 1a and b shows the equilibrium adsorption of CR onto physical-activated BA and untreated BA for various initial concentrations of CR. Both plots show a nonlinear separation pattern for favourable adsorption behaviour (Weber, 1985). It is shown that the amount of CR adsorbed per unit weight of physical-activated BA, $q_e$ increased from 19.66 to 106.61 mg $g^{-1}$ as the initial concentration of CR increases from 20-140 mg $L^{-1}$. Similar trend was observed

Table 2: Surface area of physical-activated BA and untreated BA

| Adsorbent | BET surface area ($m^2$ $g^{-1}$) |
|---|---|
| Untreated BA | 27 |
| Physical-activated BA | 134 |

Table 3: BET surface area of various adsorbents

| Adsorbent | BET surface area ($m^2$ $g^{-1}$) | Source |
|---|---|---|
| NaOH treated sawdust | 0.3742 | Mane and Babu (2011) |
| Wood shaving bottom ash (WBA) | 21.60 | Leechart *et al*. (2009) |
| Untreated BA | 27.00 | Present study |
| Physical-activated rice husk fly ash | 39.00 | Awom *et al*. (2008) |
| WBA treated with $H_2SO_4$ | 70.00 | Leechart *et al*. (2009) |
| Physical-activated BA | 134.0 | Present study |
| Unburnt coal (UC) | 290.0 | Wu *et al*. (2010) |
| Physical-activated macadamia nut-shell char | 383.0 | Awom *et al*. (2008) |
| Physical-activated sawdust fly ash | 464.0 | Awom *et al*. (2008) |
| Physical-activated bagasse bottom ash | 491.0 | Awom *et al*. (2008) |
| Physical-activated corncob nut-shell char | 781.0 | Awom *et al*. (2008) |
| Commercial activated carbon | 924.0 | Awom *et al*. (2008) |

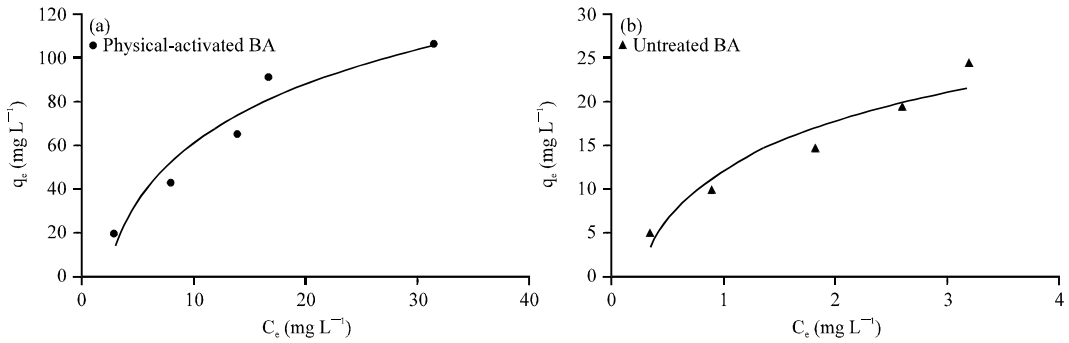



Fig. 1(a-b): Equilibrium amount of CR adsorbed onto the (a) Physically-activated BA and (b) Untreated BA

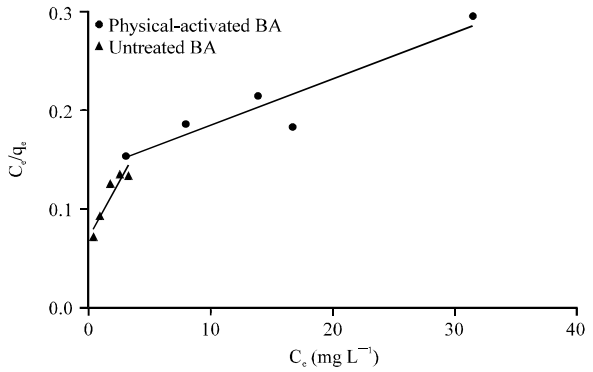



Fig. 2: Langmuir isotherm for adsorption of CR onto untreated BA and physical-activated BA

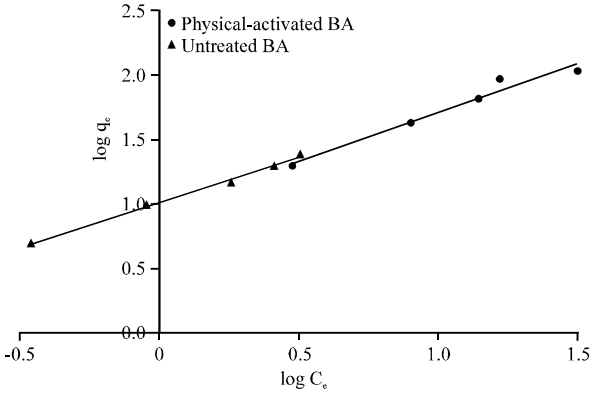



Fig. 3: Freundlich isotherm for CR adsorption onto untreated BA and physical-activated BA

Table 4: Isotherm constants for the Langmuir and Freundlich isotherm

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| Adsorbent | $Q_o$ | b | $R^2$ | $K_f$ | n | $R^2$ |
| Untreated BA | 44.64 | 0.32 | 0.89 | 10.25 | 1.43 | 0.99 |
| Physical-activated BA | 212.77 | 0.03 | 0.88 | 8.93 | 1.32 | 0.97 |

for CR adsorption onto untreated BA. The amount of CR adsorbed per unit weight of untreated BA, $q_e$ increased from 4.93 to 24.36 mg $g^{-1}$ with an increase in CR initial concentration from 25-125 mg $L^{-1}$. By comparing the two adsorbents, CR was effectively adsorbed using physical-activated BA as compared to untreated BA. This result is in agreement with the increase of adsorbent's surface area after the pyrolysis.

**Adsorption isotherm:** Figure 2 and 3 exhibits Langmuir and Freundlich isotherms plots for the adsorption of CR on untreated BA and physical-activated BA, respectively. Both figures show linearized plot of Langmuir and Freundlich models. All constants were derived from these plots and listed in Table 4. When comparing the linear correlation coefficients, $R^2$ as presented in Table 4, it can be seen that the Freundlich model yields a much better fit than the Langmuir model. The correlation coefficient, $R^2$ for untreated BA and physical-activated BA were 0.99 and 0.97, respectively by using Freundlich model while the correlation coefficient, $R^2$ for untreated BA and physical-activated BA were 0.89 and 0.88, respectively using Langmuir model. This shows that Freundlich model produces a much better fits as compared to Langmuir model. Therefore, the adsorption of CR onto both untreated and physical-activated BA is assumed to takes place at heterogeneous surface which may be attributed to the various active sites on physical-activated and untreated BA, having different affinities to CR molecules. This finding is comparable with the result reported by Vimonses *et al.* (2009) in their adsorption study of CR using zeolite. In addition, Table 5 summarizes and compares the $K_f$ constant of this present study to other contributions by several researchers on CR adsorption onto various types of adsorbents.

Table 5: Freundlich isotherm of CR adsorption onto various adsorbents

| Adsorbent | $K_f$ | References |
|---|---|---|
| Zeolite | 0.52 | Vimonses *et al.* (2009) |
| Bael shell carbon | 5.24 | Ahmad and Kumar (2010) |
| Na-Bentonite | 5.70 | Vimonses *et al.* (2009) |
| Physical-activated BA | 8.93 | Present study |
| Untreated BA | 10.25 | Present study |
| Commercial activated carbon | 20.77 | Purkait *et al.* (2007) |
| Ca-Bentonite | 26.91 | Lian *et al.* (2009) |

## CONCLUSION

Based on the result, physical activation process enhances bottom ash adsorption capacity since the adsorption capacity, $q_e$ of CR onto physical-activated BA was higher as compared to untreated BA. This showed that physical activation was able to utilize bottom ash as low cost adsorbent and provide an effective treatment for removal of dilute dyestuff from wastewater. Furthermore, the BA is freely available waste material with no additional cost since it is dumped to landfill areas. An empirical equation for heterogeneous surfaces which is Freundlich isotherm represented the experimental data better than the Langmuir isotherm.

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