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Removal of Reactive Yellow 4R Azo Dye from Synthetic Aqueous Solution by Alkali Hydrothermally Activated Fly Ash

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Highlights:

- Alkali hydrothermal activation of fly ash increases its surface area, thus increasing dye adsorption efficiency.
- The dye adsorption mechanism follows the Freundlich isotherm model.
- The dye adsorption kinetics follow the Lagergren pseudo second order model.
- Dye removal occurred primarily through surface adsorption and very little through intra-particle diffusion.

Abstract. Dye-containing wastewater affects the aesthetic quality, transparency and gas solubility of natural water bodies, hence colored wastewater must be treated before being discharged. Physical removal of dyes from wastewater can be achieved using activated carbon. However, this technique is expensive, so there is a need to find less expensive alternatives. A waste product generated from coal-fired plants known as fly ash is a sorbent that can be used to remove pollutants from solution. This study investigated the effectiveness of using alkali (NaOH) hydrothermally activated fly ash to remove Reactive Yellow 4R azo dye from synthetic aqueous solution. Na_2O in alkali hydrothermally activated fly ash increases thirteen-fold. SEM observations revealed that the raw fly ash consisted of smooth round shaped particles, whereas the activated fly ash was composed of granular crystalline particles. Batch adsorption experiments of the dye at 25 °C showed that increasing the activated fly ash quantity (0.5 to 3.5 g) increased the removal efficiency from 30% to 39.3%. The Freundlich isotherm adsorption model best described the adsorption of Reactive Yellow 4R dye by alkali hydrothermally activated fly ash with $K_F = 1.49 \times 10^{-21}$ mg/g. The dye adsorption kinetics by activated fly ash followed the Lagergren pseudo second order model, with calculated $q_e = 2.65$ mg/g; $k_2 = 0.06$ g/mg; and calculated $h = 0.42$ mg/g min^{-1}. Dye removal occurred primarily through surface adsorption and very little through intra-particle diffusion.

Keywords: *adsorption isotherm; dye removal; fly ash; kinetics; textile wastewater.*

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1 Introduction

Reactive dyes are dyes that bind to fibers through covalent bonds. Textile industries favor the use of reactive dyes due to their bright colors and light-fast, as well as water-fast characteristics; however 10-50% of dyes are discharged in effluent wastewater. Dye-containing wastewater affects the aesthetic quality, transparency and gas solubility of natural water bodies. Moreover, colored wastewater can inhibit photosynthetic activity, which could be detrimental to aquatic organisms. Hence, colored wastewater must be treated before being discharged into water bodies. Physical removal of dyes from wastewater is usually achieved using activated carbon. However, this is expensive, so there is a need to find less expensive alternatives.

A waste product from steam power plants during coal burning is fly ash. As fly ash causes environmental degradation to air and water quality, it is usually disposed in landfills. However, as more and more fly ash is being generated, there is a need to find ways to make use of fly ash to make its disposal less costly. A prospective use of fly ash is as a sorbent to remove pollutants from wastewater. Ahmaruzzaman [1] states that the physicochemical characteristics of fly ash make it an ideal adsorbent for the treatment of organic pollutants, including dyes. According to Koshy & Singh [2], chemical and hydrothermal activation of fly ash can augment its sorption capacities, as it augments its specific surface area. The use of fly ash to remove dyes from wastewater has been investigated by various authors [1,3-6], but removal of Reactive Yellow 4R dye by alkali hydrothermally activated fly ash has not been investigated yet. Table 1 summarizes the findings of these authors as compared to the present study.

Table 1 Fly ash as adsorbent for removal of reactive dyes.

Adsorbent	Findings	Ref.
Untreated fly ash	Fly ash can be used as an adsorbent to remove reactive azo dyes from wastewater. External mass transfer and intra-particle diffusion have a rate-limiting effect on the removal process, attributed to the relatively simple macropore structure of the fly ash particles. Sorption of dyes increased with increasing adsorbent dosage and decreasing particle size.	1
Untreated fly ash	Fly ash has the potential to remove Remazol Brilliant Blue (RB), Remazol Red 133 (RR) and Rifacion Yellow HED (RY) reactive dyes from aqueous solution. The amount of dye adsorbed increases with increasing initial dye concentration, contact time and temperature but decreases with particle size. The removal rate is dependent on intra-particle, as well as external mass diffusion. The adsorption fits both the Langmuir and Freundlich isotherm adsorption models. The values of the Langmuir and Freundlich isotherm constants increased with increasing temperature, these being respectively 135-180, and 15-34 mg/g for RB; 47-86, and 1.9-3.7 mg/g for RR; 37-61, and 3.0-3.6 mg/g for RY.	3

Table 1 ***Continued.*** Fly ash as adsorbent for removal of reactive dyes.

Adsorbent	Findings	Ref.
Alkali (NaOH) hydro-thermally (90 °C) activated fly ash	Alkali hydrothermal (90 °C) activation causes the fly ash surface to no longer be smooth but rough and granular, with smaller particles adhering to it. It also causes a decrease in the silica content and makes the ash more aluminum enriched. Hydrothermally activated fly ash can be used to remove Methylene Blue dye from synthetic aqueous solution, where dye removal increases with increasing sorbent dose, contact time, and pH of the wastewater. The sorption process is best described by the Langmuir isotherm model, with $q_{max} = 0.045$ mg/g. The kinetics followed the Lagergren pseudo second order model with calculated $q_e = 0.482$ mg/g, and $k_2 = 0.850$ g/mg.	4
Untreated fly ash	Fly ash was used as a sorbent to remove Malachite Green dye from wastewater. XRD analysis indicated that the raw fly ash used in the sorption experiments consisted of low-Ca Class F fly ash. Equilibrium was attained in 60 minutes. The maximum uptake of the dye occurred at a pH of 5. Percent removal of dye increased with increasing adsorbent dose. Sorption decreased with increasing temperature. The Freundlich isotherm model best described the sorption process. At temperatures of 303K, and 313K, K_f was respectively 1.547 mg/g, and 1.225 mg/g.	5
Untreated fly ash	Fly ash was used as sorbent to remove Methylene Blue, Malachite Green, and Rhodamine B dyes from textile wastewater. The removal of Methylene Blue, Malachite Green, and Rhodamine dyes varied respectively from 0.228 to 0.814; 0.219 to 0.644; and 0.184 to 0.618 mg/g when the initial dye concentration increased from 5 to 20 mg/L. Dye sorption increased with longer contact time. The sorption was best described by the Freundlich isotherm model. The values of K_F were higher for Methylene Blue, and Malachite Green dyes, these being 0.0619, 0.0777, and 0.0552 mg/g for Methylene Blue, Malachite Green, and Rhodamine B dyes respectively at a temperature of 20 °C, and 0.0655, 0.0797, and 0.0556 mg/g respectively at a temperature of 30 °C.	6
Alkali (NaOH) hydro-thermally (140 °C) activated fly ash	Based on X-ray fluorescence (XRF) and scanning electron microscope (SEM) analyses, the raw fly ash used in the experiments consisted of Class F fly ash. Alkali hydrothermal (140 °C) activation caused the surface of the fly ash to no longer be smooth but rough and granular, with smaller particles adhering to it. The silica content of the activated fly ash decreased but did not make the ash more aluminum enriched. The activated fly ash could remove Reactive Yellow 4R azo dye from synthetic aqueous solution. The sorption experiments conducted at 25 °C showed that increasing the activated fly ash quantity (0.5-3.5 g) increased the removal efficiency from 30% to 39%. The sorption of the azo dye is best described by the Freundlich isotherm model, with $K_F = 1.49 \times 10^{-21}$ mg/g. The dye sorption kinetics follow the Lagergren pseudo second order model, with calculated $q_e = 2.65$ mg/g, $k_2 = 0.06$ g/mg, and calculated $h = 0.42$ mg/g min^{-1}. Dye removal occurred primarily through surface adsorption and very little through intra-particle diffusion. Hence, although the increase in dose sorbent is seven-fold, only an increase of 9.3% in dye removal was attained.	This study

Reactive Yellow 4R azo dye (Figure 1) itself, is a single azo dye, mainly used for cotton, silk, polyamide fiber and viscose, wool fiber dying.

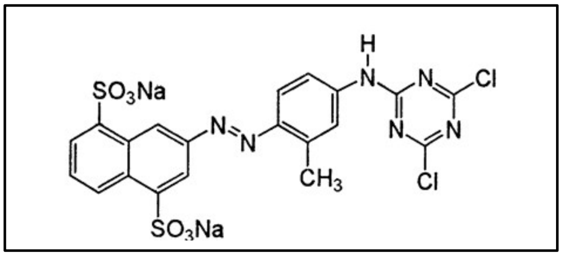


Figure 1 Reactive Yellow 4R azo dye.

This study examined the prospect of using alkali hydrothermally activated fly ash to remove Reactive Yellow 4R (RY 4R) azo dye from synthetic aqueous solution. The effect of increasing quantities of activated fly ash on dye sorption was examined, and the corresponding sorption capacity was calculated. The dye adsorption kinetics were also evaluated.

2 Experiments

2.1 Materials

The coal fly ash utilized in the experiments originated from the Labuan 2 steam power plant, Sukamaju Village, Banten, Indonesia. The raw fly ash was pulverized with a mortar, sieved at 80 mesh, and then dried at 105 °C until a constant weight was obtained.

The morphologies and compositions of the raw, and alkali hydrothermally activated fly ash were determined by scanning electron microscopy (SEM), and X-ray fluorescence (XRF) spectroscopy.

Although Ganesh, *et al.* [7] state that most dyes end up in the waste stream in hydrolyzed form, this study used the parent dye (commercial dye without any treatment), where 1 g parent dye was mixed with 1000 ml distilled water, and a dye concentration of 100 mg/L was made from the resulted solution. Dye concentrations were determined spectrophotometrically at a wavelength of 418 nm.

2.2 Activation Procedure

Coal fly ash activation was achieved through a two-step procedure adopted from Musyoka, *et al.* [8], which consisted of 1) aging, and 2) hydrothermal treatments. The aging process was achieved by mixing 20 g of raw fly ash and 20 g NaOH with 100 ml distilled water in a Teflon bottle. A magnetic bar was added, the

Teflon bottle sealed, and the mixture was stirred at 800 rpm for 48 hours at 47 °C. This was followed by the hydrothermal treatment, where the sealed Teflon container was placed for 48 hours in an oven at 140 °C and then cooled to room temperature. The mixture from the Teflon container was filtered and the filtered material was rinsed with distilled water until the filtrate's pH became 9-10. The rinsed material was dried at 90 °C for 24 hours and the dried material was kept in a sealable plastic container until needed.

2.3 Adsorption Experiments

The batch adsorption experiments were conducted at 25 °C. Varying amounts of alkali hydrothermally activated fly ash (0.5; 1.0; 1.5; 2.0; 2.5; 3.0; and 3.5 g) were mixed with 100 mg/L dye solution in Erlenmeyer flasks at 150 rpm. The solution's working volume was 150 ml. At certain time periods, samples were taken during 180 minutes, filtered, and the dye concentration was determined by spectrophotometry at a wavelength of 418 nm. The dye adsorbed by the sorbent was calculated using the following Eq. (1):

$$\frac{X}{M} = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where $\frac{X}{M}$= dye adsorbed by the activated fly ash (mg/g), C_o= initial dye concentration (mg/L), C_t = residual dye concentration at time t (mg/L), V = volume (L), and M = quantity of alkali hydrothermally activated fly ash (g).

2.4 Adsorption Isotherms

The Freundlich, and Langmuir isotherms were used to establish the mechanism of dye adsorption. The Freundlich isotherm describes less than ideal sorption on heterogeneous surfaces and is based on the assumption that as the concentration of the adsorbate augments so does the concentration of the adsorbate on the surface of the adsorbent [9]. The Freundlich isotherm mathematical equation is in Eq. (2) as follows:

$$\frac{X}{M} = K_F C_e^{\frac{1}{n}} \tag{2}$$

where K_F = approximate indicator of adsorption capacity (mg/g), $\frac{1}{n}$ = intensity of adsorption, and C_e= adsorbate concentration at equilibrium (mg/L). The slope ranges between 0 and 1, and is a degree of the intensity of adsorption or the heterogeneity of the surface, whereby it gets more heterogeneous as its value progresses closer to 0.

The Langmuir isotherm assumes that the adsorbate will form as a monolayer above a homogeneous adsorbent. Hence, when equilibrium is achieved no more adsorption will occur. It is assumed that sorption occurs at specific homogenous locations in the adsorbent and that the sorption of each molecule has identical sorption energy [10]. The Langmuir isotherm mathematical formula is:

$$\frac{X}{M} = \frac{Q_m K_L C_e}{1+K_L C_e} \tag{3}$$

where Q_m= maximum adsorption (mg/g), and K_L = the Langmuir constant associated to adsorption energy (L/mg).

2.5 2.5 Adsorption kinetics

Dye adsorption kinetics were analyzed by mixing 1.5 g activated fly ash with 100 mg/L RY 4R azo dye solution at 150 rpm. Samples were taken at various time periods in order to measure the remaining dye concentration. The mathematical equation of the Lagergren first order model is:

$$Log(q_e - q_t) = Log q_e - \frac{k_1}{2.303} t \tag{4}$$

The Lagergren pseudo second order formula is:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_e = dye adsorbed at equilibrium, q_t = dye adsorbed at time *t*, k_1 = pseudo first order rate constant, and k_2 = pseudo second order rate constant.

3 Results and Discussions

3.1 Analysis of the Fly Ash

The composition as well as the morphology of the raw and the alkali hydrothermally activated fly ash were determined by X-ray fluorescence (XRF) spectrometry, and scanning electron microscopy (SEM) analyses. The results are given in Table 2.

Table 2 Results of XRF analysis of fly ash from the Labuan 2 steam power plant.

Chemical constituent	Raw fly ash (%)	Activated fly ash (%)
SiO_2	51.95	37.71
Al_2O_3	19.45	17.28
Fe_2O_3	11.46	10.30
MnO	0.17	0.17
MgO	3.53	3.59
CaO	8.71	8.24
Na_2O	0.93	12.12

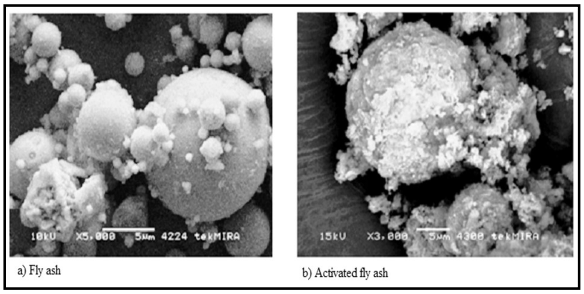
Table 2 ***Continued***. Results of XRF analysis of fly ash from the Labuan 2 steam power plant.

Chemical constituent	Raw fly ash (%)	Activated fly ash (%)
K_2O	0.65	<0.001
TiO_2	0.74	0.70
P_2O_5	0.13	0.12
SO_3	0.30	0.072
Cr_2O_3	0.013	0.009
CuO	0.008	0.003
NiO	0.007	0.004
PbO	0.005	0.002
Rb_2O	0.002	<0.001
ZnO	0.014	0.006
SrO	0.12	0.098
ZrO_2	0.050	0.053
LOI	1.76	9.40

Table 2 shows that the total of SiO_2, Al_2O_3 and Fe_2O_3 of the raw fly ash was about 82.9%. The raw fly ash was Class F fly ash given that fly ash with more than 70% $SiO_2 + Al_2O_3 + Fe_2O_3$ and a little lime is classified as low-calcium Class F fly ash [11], produced from the burning of high-rank coal (bituminous coal or anthracite) pozzolanic in character.

The SiO_2/Al_2O_3 ratio of the raw fly ash was approximately 2.67, while that of the activated fly ash was 2.18, which indicates that not much wastage of the feedstock occurred. Activation also caused a decrease in the silica content (from 51.95% to 37.71%), and an increase in Na_2O percentage from 0.93% to 12.12% (about a thirteen-fold increase) attributed to using NaOH for the aging process. It appears that the Na was incorporated into the activated fly ash, serving as a charge balancing cation. The CaO content in both the raw and activated fly ash was almost the same as Ca, also serving as a charge balancing cation [8].

The raw fly ash had a loss-on-ignition (LOI) value of 1.76%, while activation increased the LOI value to 9.40%. LOI is an important chemical parameter that represents the carbon that is still unburned. Figure 2 shows that the raw fly ash had a smooth surface, whereas that of the activated fly ash was no longer smooth but had become rough and granular in nature, with smaller particles adhering to it. These results correspond to those obtained in other earlier studies [4,8,12]. It appears that the activated fly ash's surface area increased as a result of the alkali hydrothermal treatment.



a) Fly ash

b) Activated fly ash

Figure 2 EM images of: a) raw sieved fly ash (left) and b) alkali (NaOH) hydrothermally activated fly ash (right).

3.2 Influence of Activated Fly Ash Quantity on Dye Adsorption

Examining the effect of adsorbent quantity will provide an indication of the adsorbent's ability to adsorb the adsorbate under certain abiotic conditions and provide an indication of the ability of the adsorbate to be adsorbed by the smallest quantity of sorbent. Figure 3 shows that increasing the quantity of the activated fly ash from 0.5g to 3.5g increased the dye removal percentage from about 30% to 39.3%.

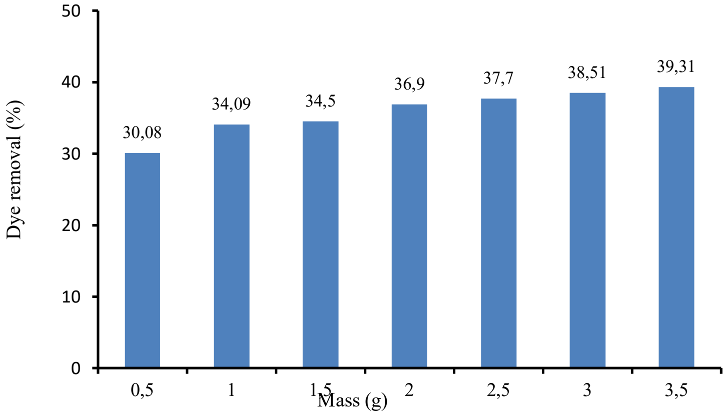
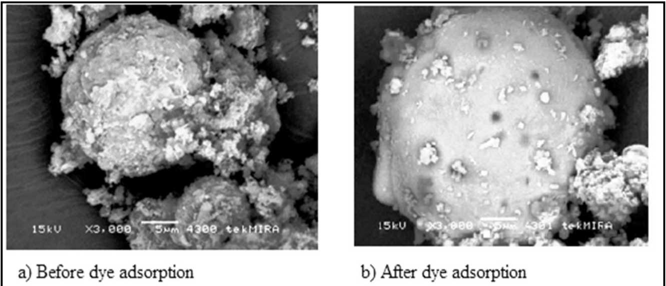


Figure 3 Effect of alkali hydrothermally activated fly ash quantity on RY 4R azo dye removal, Co = 100 mg/L, time = 180 minutes, temperature = 25 °C.

Although the increase in adsorbent dosage was seven-fold, the increase in dye removal was only 9.3%. This is attributed to dye adsorption being primarily due to surface adsorption and very little to intra-particle diffusion (see Section 3.4).

Adsorption of reactive dyes from aqueous solutions is governed by external mass transfer and intra-particle diffusion processes. The latter two have rate limiting effects on the removal process. This is attributed to the simple macropore structure of the fly ash particles [3]. However, if the adsorption process was conducted in two stages at a dose of 0.5 g adsorbent each, it may be assumed that dye removal efficiency would be enhanced and more dye would be removed.

Figure 4 presents the results of SEM imagery prior to and after dye sorption by the activated fly ash. Table 3 shows the alkali hydrothermally activated fly ash's chemical makeup. The LOI percentage after sorption increased from 9.40% to 11.87% (an increase of about 2.5%). SEM imagery (Figure 4) shows that prior to dye adsorption, the alkali hydrothermally activated fly ash had a surface that was rough and granular. After dye adsorption its surface became smoother, attributable to RY 4R azo dye molecules covering the surface (Figure 4). This is comparable to the results obtained in [13].



a) Before dye adsorption

b) After dye adsorption

Figure 4 SEM imagery of activated fly ash from the Labuan 2 steam power plant prior to (left) and after (right) adsorption of RY 4R azo dye.

Table 3 XRF analysis of alkali hydrothermally activated fly ash prior to and after adsorption of RY 4R azo dye.

Constituents	Activated fly ash (%)	Activated fly ash + adsorbed dye (%)
SiO_2	37.71	37.87
Al_2O_3	17.28	17.91
Fe_2O_3	10.30	9.63
MnO	0.17	0.16
MgO	3.59	3.70
CaO	8.24	7.67
Na_2O	12.12	10.07
K_2O	<0.001	<0.001
TiO_2	0.70	0.64
P_2O_5	0.12	0.13

Table 3 ***Continued.*** XRF analysis of alkali hydrothermally activated fly ash prior to and after adsorption of RY 4R azo dye.

Constituents	Activated fly ash (%)	Activated fly ash + adsorbed dye (%)
SO_3	0.072	0.048
Cr_2O3	0.009	0.008
CuO	0.003	0.002
NiO	0.004	0.013
PbO	0.002	0.002
Rb_2O	<0.001	<0.001
ZnO	0.006	0.007
SrO	0.098	0.093
ZrO_2	0.053	0.053
LOI	9.40	11.87

3.3 Adsorption Equilibrium

Equilibrium relationships between adsorbent and adsorbate are usually described through adsorption isotherm models. Accordingly, the experimental data obtained in the batch experiments were plotted against Freundlich and Langmuir isotherm models (Table 4).

The regression coefficients (Table 4) indicate that RY 4R azo dye adsorption by alkali hydrothermally activated fly ash best fit the Freundlich isotherm model. It therefore appears that the dye was not adsorbed as a monolayer. Moreover, the calculated Langmuir Q_m value was negative, indicating inadequacy of this isotherm model. Dzige, *et al.* [3] also reported that the Freundlich isotherm model best described the sorption of Remazol Brilliant Blue, Remazol Red 133, and Rifacion Yellow HED reactive dyes by fly ash with their K_F at 20 °C being respectively 15.54 mg/g, 1.965 mg/g, and 4.82 mg/g. The Freundlich isotherm is a model extensively used for heterogeneous systems in particular organic complexes or forms that are very interactive on activated carbon and molecular filters. It does not assume monolayer capacity but sorption on a heterogeneous surface. The Freundlich isotherm equation for RY 4R azo dye adsorption onto alkali hydrothermally activated fly ash is as follows: $q_e = 1.49x10^{-21}C_e^{11.83}$ (Table 4).

Table 4 Results of plotting experimental data against Freundlich and Langmuir isotherm models.

Freundlich isotherm			Langmuir isotherm		
n	K_F (mg/g)	R^2	Q_m (mg/g)	K_L (L/mg)	R^2
0.0845	1.49×10^{-21}	0.975	-0.318	-0.014	0.94

Then from the Freundlich equation is 0.0845, hence the $\frac{1}{n}$ value is 11.83. This suggests adsorption that is cooperative in nature, as $\frac{1}{n}$ below 1 implies chemisorption, whereas $\frac{1}{n}$ above 1 implies cooperative adsorption [14]. The adsorption capacity (K_F) was 1.49 x 10^{-21} mg/g.

3.4 Adsorption Kinetics

According to Yagub, *et al.* [15], operation of a full-scale batch process requires knowledge of dye adsorption kinetics, as this would permit determining the adsorbate uptake rate. Accordingly, the data obtained from the batch adsorption experiments were plotted against appropriate kinetic equations (Figure 5). Figure 5 and Table 5 show that RY 4R azo dye sorption is best described by the pseudo second order model, as its R^2 value was 0.99, which is greater than the value obtained for the pseudo first order model (Table 5).

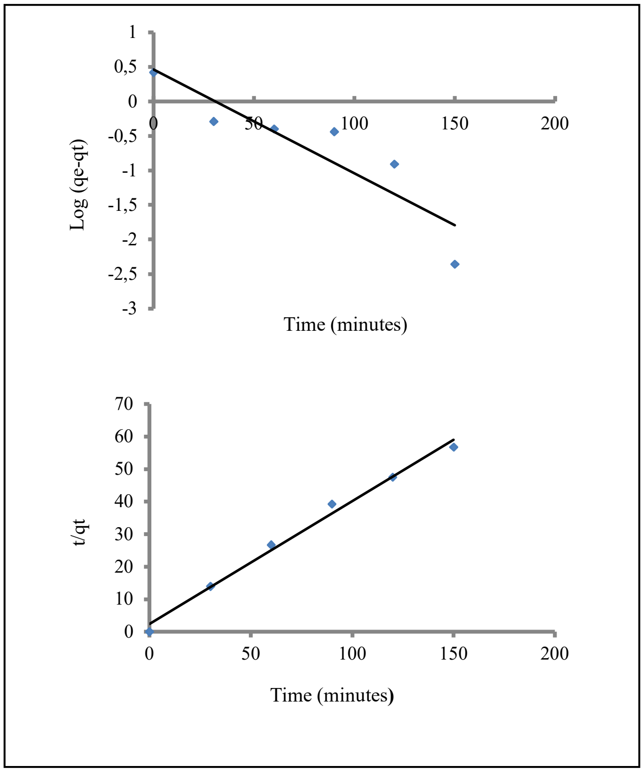


Figure 5 Pseudo first order (top) and pseudo second order (bottom) models for RY 4R dye adsorption on alkali hydrothermally activated fly ash, Co = 100 mg/L.

Table 5 Pseudo first order and pseudo second order kinetic equations of RY 4R dye adsorption by alkali hydrothermally activated fly ash, Co=100 mg/L.

Pseudo first order		Pseudo second order	
y = -0.015x + 0.465 q_e = 2.92 mg/g k_1 = -0.0345 g/min	R^2 = 0.815	y = 0.377x + 2.369 q_e = 2.65 mg/g k_2 = 0.06 g/mg.min	R^2 = 0.99

Moreover, the k_1 value of the pseudo first order model was negative, which suggests the model to be inadequate. The pseudo second order kinetics explain that the rate of adsorption is relative to the square of the number of vacant locations on the adsorbent surface. It is also proportional to the concentration of adsorbate in the solution. It can therefore be assumed that the adsorption mechanism is chemisorption [14,16-18], and that different binding locations on the activated fly ash affix the dye molecules.

Nonetheless, closer scrutiny of the results shows that the majority of RY 4R azo dye sorption occurred during the first 30 minutes of contact (Figure 6). Moreover, dye adsorption best fit the Freundlich isotherm model (Table 4), with a value of $\frac{1}{n}$ = 11.83, which indicates adsorption that is cooperative [14].

Accordingly, given the above observations, it appears that dye sorption during the first 30 minutes is due to cooperative adsorption [14] followed by chemisorption. This assumption is further reinforced by the results of the desorption analysis, where spent activated fly ash was subjected to desorption using distilled water. Only 1.59% of the dye adsorbed by the activated fly ash was released/desorbed back into the solution. The calculated q_e was 2.65 mg/g, and k_2 was 0.06 g/mg.min (Table 5). In comparison, adsorption of Methylene Blue dye on hydrothermally modified fly ash was q_e = 0.482 mg/g, and k_2 = 0.850 g/mg [4].

The pseudo second order equation can be used to determine the rate of initial dye sorption, *h* (mg/g min) [15] using the following equation:

$$h = k_2 q_e^2 \tag{6}$$

where *h* = initial dye adsorption (mg/g min), k_2 = rate constant of pseudo second order, and q_e = dye predicted to be adsorbed at equilibrium (mg/g). Accordingly, calculated *h* (initial dye adsorption) in this study was 0.42 mg/g min.

The adsorption process entails several steps. First, transport of the adsorbed molecules from the solution to the surface of the sorbent, followed by the molecules going into the sorbent's cavities. Therefore, another useful operating parameter to know is the intra-particle diffusion [15], which can be calculated as follows [19]:

$$q_{t=} K_d t^{\frac{1}{2}} \tag{7}$$

where K_d = rate constant of intra-particle diffusion (mg/g/h$^{1/2}$). In this study, K_d = 0.008 mg/g/min$^{1/2}$. This low K_d implies that dye removal occurred primarily through surface adsorption and very little through intra-particle diffusion. In comparison, K_d for Remazol Brilliant Blue, Remazol Red 133, and Rifacion Yellow HED reactive dyes (C_o = 100 mg/l) onto fly ash is 0.108, 0.037, and 0.119 mg/g/min$^{1/2}$, respectively [3]. The value of K_d for 100 mg/L Methylene Blue dye is 0.0464 mg/g/min$^{1/2}$, indicating that dye removal occurred both by surface adsorption and intra-particle diffusion [18].

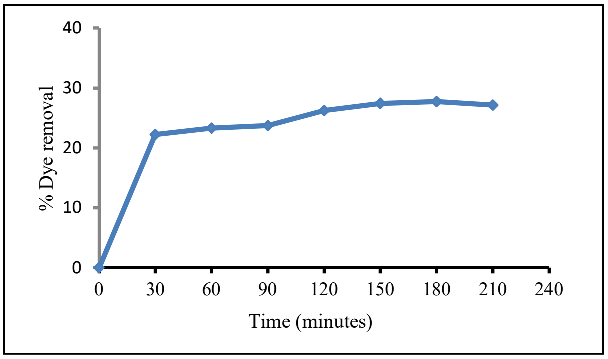


Figure 6 RY 4R dye removal (%) by alkali hydrothermally activated fly ash, C_o = 100 mg/L

4 Conclusions

This study assessed the possibility of using alkali hydrothermally activated fly ash to remove Reactive Yellow 4R azo dye from aqueous solution. The conclusions of this study are as follows: (1) the XRF analysis indicated that fly ash from the Labuan 2 steam power plant was Class F fly ash; (2) activation by alkali hydrothermal treatment did not cause wastage of the feedstock, but instead brought about a thirteen-fold increase of the Na_2O content; (3) scanning electron microscopy showed that after activation, the surface of the fly ash, which was originally smooth, became rough and granular, hence, increasing the surface area, providing more area for dye adsorption; (4) the dye adsorption batch experiments demonstrated that increasing the quantity of the activated fly ash (0.5 to 3.5 g) also increased the dye removal efficiency, with removal efficiencies ranging from 30% to 39.3%; (5) the sorption mechanism followed the Freundlich isotherm model, with $K_F = 1.49 \times 10^{-21}$ mg/g; (6) the dye adsorption kinetics followed the Lagergren pseudo second order model, with initial dye adsorption, h = 0.42 mg/g min, and K_d = 0.008 mg/g/min$^{1/2}$; (7) the low K_d value indicates that dye removal occurred primarily through surface adsorption and very little through intra-particle diffusion.

Acknowledgement

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References

[1] Ahmaruzzaman, M., *A Review on the Utilization of Fly Ash*, Prog. in Energy and Combustion Sci. **36**, pp. 327-363, 2010.

[2] Koshy, N. & Singh, D.N., *Fly Ash Zeolites for Water Treatment Applications*, J. Environ. Chem. Eng. **4,** pp. 1460-1472, 2016.

[3] Dzige, N., Aydiner, C., Demirbas, E., Kobya, M. & Kara, S., *Adsorption of Reactive Dyes from Aqueous Solutions by Fly Ash: Kinetic and Equilibrium Studies*, J. Hazard. Mater. **150**, pp. 737-746, 2008.

[4] Mor, S., Chavi, M.K., Sushil, K.K. & Ravindra, K., *Assessment of Hydrothermally Modified Fly Ash for the Treatment of Methylene Blue Dye in the Textile Industry Wastewater,* Environ. Dev. Sustain, **20** (2), pp. 625-639, 2018.

[5] Dwivedi, M.K., Tripathi, L.P. & Dwivedi, A.K., *Sorption Studies on Removal of Malachite Green from Wastewater by Coal fly ash***,** IJSR, **3,** pp. 57- 60, 2014.

[6] Khan, T.A., Ali, I., Singh, V. & Sharma S., *Utilization of Fly Ash as Low-Cost Adsorbent for the Removal of Methylene Blue, Malachite Green and Rhodamine B Dyes from Textile Wastewater***,** JEPS, **3**, pp. 11-22, 2009.

[7] Ganesh, R., Boardman, G.D., & Michelsen, D., *Fate of Azo in Sludges,* Wat. Res., **28** (6), pp. 1367-1376, 1994.

[8] Musyoka, N.M., Petrik, L.F., Balfour, G., Misheer, N., Gitari, W. & Mabovu, B., *Removal of Toxic Elements from Brine Using Zeolite Na-P1 Made from a South African Coal Fly Ash*, in International Mine Water Conference Proceedings, pp. 680-687, 2009.

[9] Freundlich, H., *Adsorption in Solution,* Phys. Chemie, **57**, pp. 384-410, 1906.

[10] Langmuir, I., *Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum.,* J. Am. Chem. Soc., **40**, pp. 1361-1403, 1918.

[11] *ASTM Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* (C618-05), in Annual Book of ASTM standards. **04.02,** 2005.

[12] Murayama, N., Yamamoto, H. & Shibata, J., *Mechanism of Zeolite Synthesis from Coal Fly Ash by Alkali Hydrothermal Reaction,* Int. J. Miner. Process, **64**, pp. 1-17, 2002.

[13] Kara, S., Aydiner, C., Demirhas, E., Kobya, M. & Dizge, N., *Modeling the Effects of Adsorbent Dose and Particle Size on the Adsorption of Reactive Textile Dyes by Fly Ash*, Desalination, **212,** **pp.** 282-293, 2007.

[14] Haghseresht, F & Lu, G.Q., *Adsorption Characteristics of Phenolic Compounds onto Coal-Reject-Derived Adsorbents,* Energy & Fuels**, 12**(6), pp. 1100-1107, 1998.

[15] Yagub, M.T., Sen, T.K., Afroze, S. & Ang, H.M., *Dye and Its Removal from Aqueous Solution by Adsorption: A Review*, Adv. Colloid Interface Sci., **209,** pp. 172-184, 2014.

[16] Qui, H., LV, L., Pan, B-C., Zhang, Q, Zhang, W. & Zhang, Q., *Critical Review in Adsorption Kinetic Models*, J. Zheijang Univ. Sci. A, **10**(5), pp. 716-724, 2009.

[17] Huang, W-J., Li, D., Liu, Z-Q., Tao, Q., Zhu, Y., Yang, J. & Zhang, Y-M, *Kinetics, Isotherm, Thermodynamic, and Adsorption Mechanism Studies of La(OH)*$_3$*-Modified Exfoliated Vermiculites as Highly Efficient Phosphate Adsorbents,* Chem. Eng. J., **236,** pp. 191-201, 2014.

[18] Kumar, K.V., Ramamurthi, V. & Sivanesan, S., *Modeling the Mechanism Involved During the Sorption of Methylene Blue onto Fly Ash,* J. Colloid Interface Sci., **284,** pp. 14-21, 2005.

[19] Weber, W. & Morris, J., *Kinetics of Adsorption on Carbon from Solution*, J. Sanit. Eng. Div., **89**(2), pp. 31-60, 1963.