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COLOR REMOVAL FROM PULP MILL EFFLUENT USING COAL ASH PRODUCED FROM GEORGIA COAL COMBUSTION PLANTS

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Abstract

In this study, Coal Fly Ash (CFA), a byproduct of coal combustion power plants, was used as an adsorbent to remove color from locally-obtained pulp mill effluent (PME). Batch adsorption studies were conducted to determine the adsorption parameters that would result in the maximum color removal from PME at the lowest CFA dosage and process cost. The effects of operating variables on color removal were studied by varying: 1) CFA dosage, 2) initial PME pH, and 3) contact time. The findings indicate that the optimum CFA dosage for cost-effective color removal was 100.0 g/L (80.5% removal) given an initial effluent color concentration below 900 mg/L Pt-Co color units. For effluent samples with a color concentration over 900 mg/L Pt-Co color units, the optimum CFA dosage was 250.0 g/L (80.4% removal). In addition, no pH adjustment of the PME was required for maximum color removal. A kinetic study showed that color removal by CFA occurred rapidly in the first hour, and adsorption equilibrium was achieved at 24 hours. Additionally, the kinetic and isotherm adsorption data was best described by the Ho et al. kinetic model and the Langmuir and Freundlich isotherm models, respectively. Overall, this research found CFA to be a promising low-cost adsorbent for the removal of color from PME.

Keywords: adsorption, Coal Fly Ash (CFA), color removal, Pulp Mill Effluent (PME)

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1. Introduction

Historically, one of the worst polluters in the United States has been the pulp-making industry. Pulp mills in the US produce 58 million tons of pulp annually, and are the largest industrial consumer of fresh water (Department of Energy, 2005; EPA, 1997). For every ton of pulp produced, chemical pulp mills discharge approximately 114,000 liters of effluent containing numerous organic/inorganic pollutants and coloring compounds (Energetics Incorporated, 2005; Pokhrel and Viraraghavan, 2004). The Clean Water Act of 1977 placed stringent restrictions on effluent concentrations of substances proven to be either acutely or chronically hazardous, such as chlorinated organic compounds, but other unregulated compounds still pose an environmental concern. One such concern in secondary pulp mill effluent (PME) is color, which is composed of lignin and other organics extracted from wood fibers during the pulping process. In addition to degrading the aesthetics of rivers and streams, color in PME is known to interfere with light transmittance in aquatic ecosystems (Paper Task Force, 1995). This, in turn, reduces the production of dissolved oxygen via photosynthesis and diminishes the "self-purification capacity" of bodies of water (Jain et al., 2009).

Prior to discharge into surface waters, PME must undergo physical (primary) and biological (secondary) treatment to reduce toxic compounds to permissible levels. Physical treatment is used to remove suspended solids, while biological treatment uses oxygen and microorganisms to remove high concentrations of Biochemical Oxygen Demand (BOD) (Environment Canada, 2003). Not all PME contaminants are biodegradable, so the biological

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treatment stages have a very limited effect on toxicity and color (Catalkaya and Kargi, 2007; Pokhrel and Viraraghavan, 2004; Shawwa et al., 2001; Vergara-Fernandez et al., 2017). These compounds can be removed by tertiary treatment processes such as adsorption and coagulation/flocculation, but mills rarely use these due to the cost involved and lack of discharge regulations for color (Environment Canada, 2003).

Amongst pulp mills that employ tertiary membrane filtration, treatment, ozonation, coagulation/flocculation, and adsorption are the predominant methods used (Ali et al., 2013). Membrane filtration, though effective at removing color, is only suitable for low-volume effluent streams cost of treatment because the increases proportionately with volume of fluid treated (Johnson et al., 2012). Chemical treatment methods, such as coagulation/flocculation and ozonation, can effectively remove color with materials that cause specific chemical reactions. However, these processes are expensive to implement, and often result in undesirable byproducts requiring an additional treatment step (El-Fadel et al., 2012). One of the main drawbacks of coagulation/flocculation is the high quantity of sludge generated, which is difficult to dispose of (Jain et al., 2009). Ozonation treatment requires high energy/chemical input, and is markedly less efficient at high dosages of ozone (Hodur et al., 2018; Johnson et al., 2012; Lagos et al., 2009). The most attractive treatment option to pulp mills for removing PME color is adsorption, and predominantly using activated carbon. Unfortunately, this material is very expensive to procure and the treated effluent must be subsequently filtered to remove any remaining powdered activated carbon (Johnson et al., 2012).

Due to the high cost of activated carbon, there is an emerging body of research characterizing various low-cost adsorbents (LCAs) alternatives to activated carbon that are easily obtainable by wastewater treatment facilities (Singh et al., 2003). One such material in particular shows promise: Coal Fly Ash (CFA), the combustion byproduct of coal-burning power plants. CFA is an effective adsorbent because the ash particles have high specific surface area and porosity (Ahmaruzzaman, 2010). Because adsorption occurs on both internal and external surfaces of an adsorbent, materials with high surface area per unit mass may possess high adsorption capacities. High specific surface area also has a positive correlation with an adsorbent's porosity, and both properties heavily influence adsorption capacity (Wang et al., 2008).

A collection of studies performed within the last decade report the successful removal of color and related compounds from wastewater by CFA (Andersson et al., 2012; Prasad and Srivastava, 2009; Wang and Wu, 2006). CFA has also been successfully used to remove reactive dyes (Remazol Brilliant Blue, Remazol Red 133, and Rifacion YellowHED), as well as anionic dyes (Acid Black 1, Acid Blue 193) (Dizge et al., 2008; Sun et al., 2010). In addition, CFA has been found to effectively adsorb various chlorophenols in a laboratory setting (Blissett and Rowson, 2012). The simultaneous removal of both color and hazardous organics (such as chlorophenol) from PME by CFA, at a significantly reduced cost, would be enormously beneficial to the ecosystems of receiving waters. Moreover, the environmental engineering community is searching for additional constructive uses for CFA since its disposal can be extremely costly and represents a serious environmental concern. The proposed solution is to utilize these two waste products synergistically via adsorption to cost-effectively mitigate the environmental hazards posed by both CFA and PME.

Color is not the only substance removed during adsorption; various other organic compounds may also be removed. Therefore, the disposal of the spent CFA adsorbent must also be considered, because the adsorbed compounds cannot be allowed to re-enter the environment. One option for spent CFA disposal is submitting it for use in fly ash lightweight aggregate, a material used in concrete (Wei et al., 2011). Production of the aggregate includes a sintering step, where the fly ash is heated to 1200°C to form aggregate pellets (Brickwell). At this temperature, organic compounds retained by CFA are oxidized and removed from the CFA's surface. This process is similar to the regeneration process for activated carbon, where adsorbed are destroyed by high temperatures (EPA, 2000). Other authors have also suggested burning fly ash at elevated temperatures as a disposal method. In their article, Kushwaha et al. (2010), examined the oxidation behavior of activated carbon and bagasse fly ash up to 1,000°C in a thermogravimetric analysis. They concluded that bagasse fly would be suitable for use in a high temperature furnace. Therefore, the disposal of spent CFA will not be a serious obstacle to its use as an adsorbent in a wastewater treatment operation.

The goal of this research was to maximize PME color removal with the minimal amount of CFA. Color removal was investigated by varying four adsorption parameters in batch studies: 1) Dosage of CFA; 2) Initial pH of the PME; 3) Contact time; and 4) CFA particle size. Isotherm studies were also completed by using the optimal color removal parameters defined in preceding experiments. Existing kinetic and isotherm models were used to describe the observed adsorption results.

2. Materials and methods

2.1. Materials

The secondary PME samples for this research were collected at an operating bleached softwood Kraft mill in Georgia. This mill produces bleached Kraft pulp for absorbent applications. It is also important to note that the secondary PME sample was collected at the discharge point of a conventional aerated stabilization basin, an activated sludge biological treatment process for the mill's effluent. The secondary PME samples were stored at room temperature $(20\pm1^{\circ}C)$ in the Water and Environmental Research Lab at Georgia Southern University until needed for testing.

CFA samples were supplied by Boral Material Technologies, which is the exclusive contractor handling CFA disposal for Georgia Power. The ash was collected from the Georgia Power, Plant Bowen, a coal-burning power plant in north Georgia. The chemical composition of the Class F CFA was determined from the MSDS included with the sample, and is shown in Table 1 (Boral Material Technologies, 2007).

 Table 1. Chemical composition of the locally-collected

 CFA sample

Compound		Mass Percentage (%)		
Silica	SiO ₂	40 - 60		
Aluminum oxide	Al ₂ O ₃	18 - 31		
Iron oxide	Fe ₂ O ₃	5 - 25		
Calcium oxide	CaO	1 - 6		
Magnesium oxide	MgO	1-2		
Titanium oxide	TiO ₂	1 - 2		
Inorganic arsenic		16 – 210 ppm		

2.2. Sample analysis methods

The sieve analysis was completed using a Ro-Tap RX-29 Sieve Shaker and Fisher ASTM E 11 test sieves (ASTM, 2015). The specific sieve sizes used were: Nos. 10, 18, 35, 50, 100, and 325 with the sieve openings of: 2.00 mm, 1.00 mm, 0.50 mm, 0.297 mm, 0.15 mm, and 0.044 mm (44 μ m), respectively. A Hach DR 5000 Spectrophotometer was used to measure the true color of the PME samples following to the Hach Method 8025: *Color, True and Apparent*, which complies with ASTM D 1209 – 05. True color is a measure of the absorbance of light at the 455 nm wave-length by dissolved color molecules (ASTM, 2011) and expressed as mg/L Pt-Co color units. The amount of color adsorbed per unit mass of CFA was calculated using Eq. (1).

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where: q_e is adsorption capacity (mg/g), C_i is the initial color concentration (mg/L Pt-Co color units) of PME, C_e is the final color concentration (mg/L Pt-Co color units) of PME, M is the mass of CFA used (g), and V is the volume of PME (L) (Hameed et al., 2008).

The pH of untreated and treated PME samples was measured using an Orion 720A pH meter with an Orion 8102BN pH probe. A three-point instrument calibration was performed by measuring the pH of 4.0, 7.0, and 10.0 pH standard buffer solutions and adjusting the settings as necessary. The pH meter was calibrated prior to each batch of sample measurements. The measurement of chemical oxygen demand (COD) was completed using the Hach DR5000 Spectrophotometer and Hach Method 8000, which complies with ASTM D1252-06 (ASTM, 2012). Only select samples from each batch were measured for COD concentration.

2.3. Adsorption batch studies

Batch study experiments were carried out to measure the adsorption characteristics of PME color on CFA. Experimentation consisted of combining 100 mL of secondary PME and a measured quantity of CFA in a 250 mL conical Erlenmeyer flask and covering the flask with laboratory film. Each batch of flasks was mixed at 150 RPM on a Thermo Scientific MaxQ 3000 Orbital Shaker for a predetermined time at a room temperature of $(20 \pm 1^{\circ}C)$. After mixing, the CFA was separated from the treated PME by vacuum filtering the mixture through 0.45 µm Pall membrane filter paper. Immediately after filtration, the color concentration, pH, and temperature of each sample was measured. In all batch study experiments, duplicate flasks with identical CFA and effluent mixtures were used to represent each sample. Color and pH measurements were taken from each flask, and the average reading between the two identical samples was used for data analysis. In addition, blank samples with no CFA were also run in each batch study to determine the impact of mixing and filtration on color removal.

The effect of CFA dosage on color removal was studied by varying the dosage from 0.1 to 100.0 g/L CFA, for a duration of 6 hours. The dosage CFA corresponding to an 80% reduction in PME color was declared as the optimum dosage. Later experimentation showed that a higher CFA dosage range was required to achieve 80% color removal when the color concentration of the effluent exceeded 900 mg/L Pt-Co color units. Therefore, additional batch studies were completed at a dosage range of 100.0 to 350.0 g/L CFA to determine the optimum dosage at higher effluent color concentrations. The effect of initial effluent pH on color removal was investigated by varying the pH from 4 to 12 during four separate batch experiments (6 hours), each at a different CFA dosage. PME pH was adjusted using either 3 M HCl or 5 M NaOH solution. Net color removal was determined by subtracting the final color concentration of pH-adjusted blanks from that of samples treated with CFA. It was observed that initial effluent pH did not significantly affect effluent color removal; therefore, subsequent batch experiments were conducted without pH adjustment.

Kinetic studies were performed by varying the PME and CFA contact time at three different CFA dosages. Samples were taken at predetermined intervals. For the third kinetic batch study, samples were collected at smaller time intervals (every 5 minutes versus every 30 minutes). This allowed the transient behavior of color removal by CFA to be observed in more detail. The kinetics of the adsorption were described using the Lagergren, and Ho and Mckay kinetic models (Lagergren, 1898; Ho and Mckay, 1999). Isotherm studies were conducted by

varying the CFA dosages from 100.0 to 350.0 g/L, and collecting samples after equilibrium was attained at 24 hours. The Langmuir and Freundlich isotherms were used to describe the observed adsorption phenomena at equilibrium (Freundlich, 1906; Langmuir, 1916).

3. Results and discussions

3.1. Characterization of the PME

The physicochemical characteristics of the secondary effluent samples obtained from the pulp mill are presented in Table 2. Effluent pH remained relatively constant across the four samples collected. In addition, there was a distinct correlation between color and COD in the raw effluent; higher levels of color corresponded with higher COD.

3.2. Effect of CFA dosage

Fig. 1 shows the results of the experiment at the low CFA dosage range. As the dosage was increased from 0.1 to 2.0 g/L CFA, the percent color removal remained nearly constant at 5%. Beginning at 2.0 g/L, a linear relationship between CFA dosage and percent color removal develops. The PME color removal target of 80% was achieved with a CFA dosage of 100.0 g/L, which was established as the optimum dosage for further experiments.

After collecting the third PME sample from the participating pulp mill, a significantly higher concentration of color than earlier PME samples was observed (887 vs. 571 mg/L Pt-Co color units). To maintain a removal efficiency of 80% in further batch studies, a higher CFA dosage was deemed necessary.

The results of the high-range CFA dosage experiments are shown in Fig. 2. The linear relationship found in earlier studies continues into the high dosage range, and at 250.0 g/L CFA, 80% color removal was achieved. For the later batch studies where the PME color concentration exceeded 900 mg/L Pt-Co color units, a CFA dosage of 250.0 g/L was used.

The effective CFA dosage for color removal found in this study is comparable to effective dosages found in similar studies. Zaharia and Suteu (2013) reported the effective CFA dosage that resulted in 30% color removal from textile mill effluent was 40.0 g/L. Prasad and Srivastava (2009) noted the most effective CFA dosage was 100.0 g/L CFA, which resulted in 91% color removal. Another relevant study, completed by Andersson et al. (2012), found an effective CFA dosage for the removal of lignin from effluent PME to be 300.0 g/L. At that dosage, they observed 97% lignin removal from the effluent.

3.3. Effect of PME pH

Fig. 3 shows the net color removal at various PME pH values for each CFA dosage tested. Overall, it observed that altering the initial PME pH did not significantly affect the removal of color by CFA. One notable exception occurred at a CFA dosage of 20.0 g/L and initial effluent pH of 4.0, where net color removal was markedly higher (49%) than at other pH values. For pH 6.0 - 12.0 (at 20.0 g/L CFA), there was little variation in removal; the average net color removal was $14 \pm 2\%$. Because the observed color removal at 20.0 g/L CFA did not meet the research goal of 80%, higher dosages were used in subsequent batches.



Table 2. Physicochemical properties of locally-collected secondary pulp mill effluent



Fig. 1. CFA dosage (low range) vs. percent color removal at an initial PME color concentration of 571 mg/L Pt-Co color units



Fig. 2. CFA dosage (high range) vs. percent color removal at an initial PME color concentration of 928 and 1039 mg/L Pt-Co color units, respectively



Fig. 3. Effect of initial PME pH on net percent color removal at four CFA dosages

Net color removal increased from pH 4.0 to 6.0, then decreased from pH 6.0 to 8.0, and finally increased again as pH became more basic. The results showed that an initial PME pH of 6.0 - 7.0 would yield the maximum amount of color removal. However, for the CFA dosages studied, net color removal tended to vary by only \pm 5% across the pH range, indicating the extra effort and cost incurred by pH adjustment didn't result in a significant improvement. In support of this finding, Prasad and Srivastava (2009) also found that initial PME pH had minimal effect on color removal by CFA. They reported the most effective pH to be 7.0 for color removal from distillery spent wash. Therefore, the PME's unaltered pH of 8.0 - 9.0 was used for the subsequent batch studies in this research.

3.4. Kinetic study and kinetic models

The kinetic aspects of PME color adsorption on CFA were examined by varying the contact time from

0 to 48 hours at three different CFA dosages. The resulting percentage color removal as a function of time is shown in Fig. 4. For all three dosages, color removal exhibited a similar relationship to contact time; wherein color was quickly adsorbed during the first hour of contact, and became asymptotic after 24 hours. For the first batch of the samples with a low dosage of 100.0 g/L CFA, the initial spike of color removal in the data indicated that adsorption of color occurred quickly. Within the first hour of contact, the color removal from the effluent rapidly climbed to 35%, and then began to plateau at 12 hours of contact. After 24 hours, no significant additional color removal occurred, therefore, an adsorption equilibrium time of 24 hours was established.

For both the second and third batch of samples, higher CFA dosages of 250.0 and 200.0 g/L were used, respectively. These dosages were previously found to be effective given a PME color concentration over 900 mg/L Pt-Co color units. At a dosage of 250.0 g/L CFA,

a 15-minute contact time resulted in 71% of PME color removal. By 24 hours, effluent color removal increased to 84%; color removal began to plateau after this point. The rapid rate of adsorption may be attributed to the high initial concentration gradient of the color in PME versus on the surface of CFA particles. In essence, all sites on the adsorbent (CFA) surface were at first vacant, but as these sites became quickly occupied by the adsorbate (color), further adsorption of color requires diffusion of effluent into the pores of the adsorbent (Shahmohammadi-Kalalagh et al., 2011). The third batch was treated with a slightly lower CFA dosage of 200.0 g/L to slow the rate of adsorption. In addition, the sampling intervals during the first hour of the experiment were decreased to observe the initial phase of the reaction in more detail. The experimental data show a trend similar to the other batches: color removal transpired rapidly during the first hour, and reached the equilibrium at 24 hours. The equilibrium time for determined in the first batch was thus confirmed to be 24 hours.

All three batches tested were characterized by the rapid removal of color by CFA in the first 60 minutes of contact. For example, over 50% of the color was removed from the PME samples in the first five minutes (at a CFA dosage of 200.0 g/L). This observation mimics the adsorption kinetics of CFA reported by Zaharia and Suteu (2013). Sun et al. (2010) noted that reactive red dye was rapidly removed by CFA within 20 minutes of contact, after which there was only a gradual increase in dye removal.

The Lagergren pseudo-first order and Ho and McKay pseudo-second order kinetic models were used to model the rate of color adsorption based on CFA's adsorption capacity. These models were identified in the literature as being the most applicable to color removal by CFA (Ho and McKay, 1999; Ho, 2006). The Lagergren pseudo-first order equation is (Eq. 2) (Lagergren, 1898):

$$q_t = q_e (1 - e^{-k_1 t})$$
 (2)

The Lagergren rate constant of pseudo-first order adsorption, k_1 (1/h), is determined from the linear plot of $log (q_e - q_t)$ vs t, using the linear form of Lagergren's equation (Eq. 3) (Hameed et al., 2008).

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303}$$
(3)

The Ho and McKay (1999) pseudo-secondorder kinetic equation is (Eq. 4):

$$q_{t} = \frac{q_{e}^{2}k_{2}t}{1 + q_{e}k_{2}t}$$
(4)

The second-order rate constant, k_2 (g/mg·h) is determined in the same manner as pseudo-first-order model. Likewise, the linear form of Eq. (4), is expressed as (Eq. 5):

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t$$
(5)

This equation may also be used to obtain a value for k_2 from the plot of t/q_t vs t (Hameed et al., 2008; Ho, 2006). Both kinetic models were evaluated for the adsorption of color onto CFA to determine their applicability to these materials. Microsoft Excel was used to generate the linear regression equations.



Fig. 4. Effect of contact time on color removal from PME at three CFA dosages

Fig. 5 shows observed q_e values plotted against q_e values predicted by the Lagergren pseudo-first order model. The Lagergren constants estimated by the regressions are listed in Table 3. Theoretical adsorption capacity (q_e) values for CFA estimated by the linear regressions ranged from 0.47 - 2.02 mg/g. The R^2 values ranging from 0.83 to 0.94 for the linear estimation of the Lagergren pseudo-first order equation constants indicate a satisfactory fit with observed data. However, the t-test showed that the estimated q_e value at a dosage of 250.0 g/L CFA was not statistically significant at the 95% confidence level. All other Lagergren equation constants estimated by the regression were statistically significant at the 95% confidence level. Therefore, the Lagergren pseudo-first order kinetic model provides an acceptable description of the observed adsorption kinetics. There is some agreement with this conjecture in the literature, as Prasad and Srivastava (2009) reported the Lagergren pseudo-first order kinetic model satisfactorily describe the adsorption of color from distillery effluent onto CFA.

The Ho and McKay (1999) pseudo-second order kinetic model, in contrast, exhibited a very close fit to the data. Theoretical adsorption capacity (q_e) values for CFA estimated by the linear regression ranged from 2.78 - 3.29 mg/g. A linear plot of experimental and model-predicted kinetic data is shown in Fig. 6, and pseudo-second model constants are presented in Table 3. For all three sample batches, the coefficient of determination values (R^2) values met or exceeded 0.99. The *t*-test confirmed that the linear estimation of the Ho et al. pseudo-second order kinetic constants were statistically significant at the 95% confidence level. Between the two kinetic models evaluated in the current research, the Ho et al. pseudosecond order kinetic model describes the adsorption kinetics of PME color onto CFA better than the Lagergren pseudo-first order kinetic model. Prasad and Srivastava (2009) stated in their evaluation of kinetic models for color adsorption by CFA that the Ho and McKay (1999) pseudo-second order kinetic model provided the best fit to the observed kinetic study data.



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Fig. 5. Experimental values plotted against values predicted by the linear form of the Lagergren pseudo-first order kinetic model



Fig. 6. Experimental values plotted against values predicted by the linear form of the Ho and McKay (1999) pseudo-second order kinetic model

Kinetic Model	Constant	100.0 g/L CFA		200.0 g/L CFA		250.0 g/L CFA	
		Estimate	P level	Estimate	P level	Estimate	P level
Lagergren Kinetic Model	$q_e(mg/g)$	2.02	0.000	0.47	0.000	0.93	0.434
	k ₁ (1/h)	0.013	0.002	0.048	0.000	0.114	0.000
	R ²	0.830	-	0.879	-	0.936	-
Ho et al. Kinetic Model	$q_e(mg/g)$	2.78	0.007	3.01	0.001	3.29	0.050
	k ₂ (g/mg·h)	0.42	0.000	0.84	0.000	1.17	0.000
	R ²	0.999	-	0.999	-	0.999	-

 Table 3. Lagergren pseudo-first order and Ho and McKay (1999)pseudo-second order kinetic model constants and statistical parameters for color removal by CFA

3.5. Isotherm study and isotherm models

Well established isotherm models were used to describe the adsorption equilibrium. During a review of the literature, the Langmuir and Freundlich adsorption isotherms were suggested as most applicable to CFA (Ho, 2004; Foo and Hameed, 2010). The Langmuir model (Langmuir, 1916) is based on two general assumptions about the adsorption process: 1) adsorbate molecules are adsorbed onto the surface of the adsorbent in a single layer and 2) this phenomenon takes place at a finite number of suitable sites that do not interact with each other. Eq. (6) gives the general form of the Langmuir equation.

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \tag{6}$$

where C_e is the equilibrium concentration of color (mg/L Pt-Co color units), q_e is the mass of color adsorbed per gram of CFA at equilibrium (mg/g) (ASTM, 2011). Q_0 (mg/g) and b (L/mg) are Langmuir constants determined by performing a regression analysis. The former constant is defined as "maximum monolayer coverage capacity" (Dada et al., 2012), in essence the maximum theoretical adsorption capacity. Constant b is related to the energy or rate of adsorption (Bhattacharya et al., 2008; Hameed et al., 2008). For the linear regression analysis of the isotherm, the linearized Langmuir equation was used (Eq. 7):

$$\frac{C_{e}}{q_{e}} = \frac{1}{Q_{0}b} + \frac{C_{e}}{Q_{0}}$$
(7)

The linear plot of the Langmuir isotherm was generated by plotting (C_e/q_e) vs C_e . The observed and Langmuir model predicted values for C_e and q_e are shown in Fig. 7. Values for Q_0 and b estimated by the linear regression, along with correlation values, are presented in Table 4. The Langmuir model was found to fit the experimental data quite well, as indicated by favorable R^2 values of 0.99. Furthermore, the t-test showed that the linear estimation of the Langmuir constants was statistically significant at the 95% confidence level. A generalized characterization of the Langmuir constants can be made by calculating the constant separation factor, R_L , using Eq. (8).

$$R_L = \frac{1}{1 + bC_e} \tag{8}$$

The value of R_L characterizes the adsorption as either: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Foo and Hameed, 2010). All R_L values listed in Table 4 fall between 0.92 and 0.94, indicating the adsorption of color by CFA is favorable.

Other studies that investigated the use of CFA for color removal have also reported that the adsorption of color onto CFA follows the Langmuir isotherm model. For the adsorption of color from spent distillery wash onto CFA, Prasad and Srivastava (2009) reported Langmuir constants of 0.00194 L/mg (*b*) and 85.2 mg/g (Q_0). Similarly, Andersson et al. (2012) determined these values to be 0.0017 L/mg (*b*) and 28 mg/g (Q_0) for PME color removal by CFA. The agreement between the *b* values reported in the literature and those found in the present research (the estimated values for *b* fell between 0.012 and 0.028 L/mg) means that during adsorption, color likely exhibits monolayer coverage of CFA particles.

The adsorption capacities of CFA and other Low Cost Adsorbents (LCAs) for PME color removal are compared in Table 5. Black wood ash (Tantemsapya et al., 2004) exhibited an adsorption capacity similar to CFA, indicating that these materials likely have a similar chemical composition and surface structure.

The reported adsorption capacity of bagasse fly ash (BFA) (Jain et al., 2009) and water hyacinth-based activated carbon (WHAC) (Boonpoke, 2015) are significantly higher than that of CFA. This can be attributed to higher carbon content in BFA (16%) and WHAC (16.3%) as well as higher specific areas of 450 m²/g and 1504 m²/g for BFA and WHAC, respectively. In contrast, the average values reported in the literature for CFA's carbon content and specific surface area were 11.2% and 5.36 m²/g, respectively (Wang et al., 2008).

The Freundlich isotherm (Freundlich, 1906) is primarily used to describe non-ideal adsorption processes for powdered adsorbents (Bhattacharya et al., 2008), often in conjunction with organic/inorganic adsorbates (Hsu, 2008). In contrast to the Langmuir model, the Freundlich model assumes multilayer adsorption occurs, rather than monolayer.



Fig. 7. Experimental values plotted against values predicted by the linear Langmuir isotherm model. C_i denotes the initial concentration of color in the effluent

Table 4. Langmuir and Freundlich constants and statistical parameters for color removal by CFA

Isotherm Model	Constant	$C_i = 928 mg/L$		$C_i = 1036 \ mg/L$	
		Estimate	P level	Estimate	P level
Langmuir Isotherm	$Q_0 (mg/g)$	4.15	0.003	3.23	0.034
	b (L/mg)	0.018	0.000	0.028	0.000
	RL	0.98	-	0.99	-
	\mathbb{R}^2	0.989	-	0.990	-
Freundlich Isotherm	$K_F (mg/g (L/mg)^{1/n})$	1.21	0.159	1.25	0.034
	1/n	0.184	0.000	0.144	0.004
	\mathbb{R}^2	0.913	-	0.721	-

Table 5. Comparison of color removal and adsorption capacity for CFA and various LCAs

Adsorbent	Effective Dosage (g/L)	Effluent Color (mg/L)	% Color Removal	Adsorption Capacity (mg/g)
Black Wood Ash	20	2300	42.2%	20.53
Bagasse Fly Ash	2	-	86%	88.5
Hyacinth-based Carbon	5	831	97%	129.87
GA Power Fly Ash	250	928	80%	4.15

It also assumes "a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface" (Noonpui et al., 2010). The Freundlich isotherm equation is (Eq. 9):

$$q_e = K_F C_e^{1/n} \tag{9}$$

where: K_F (mg/g (L/mg)^{1/n}) and *n* are Freundlich constants (Freundlich, 1906). K_F is defined in the literature as the "adsorption or distribution coefficient" (Sun et al., 2010) and represents adsorption capacity (Foo and Hameed, 2010). Constant *n* corresponds with adsorption intensity (Sun et al., 2010). Eq. (10) is the linear form of the Freundlich equation.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{10}$$

The linear plot of the Freundlich isotherm, shown in Fig. 8, was generated by plotting $log(q_e)$ vs $log(C_e)$. A linear regression of the data was used to estimate the values of the Freundlich constants K_F and *n*, which are listed in Table 4, along with correlation values. The slope of the linear Freundlich equation, 1/n, ranges from 0 to 1, and as its value approaches 0, the adsorbent surface is characterized as being increasingly heterogeneous. Lower 1/n values indicate favorable adsorption phenomena (Foo and Hameed, 2010). The R^2 values for the linear estimation of the Freundlich equation were lower than those of the Langmuir model, indicating a less favorable fit to the data. In addition, the t-test showed that the linear estimations of the Freundlich constant K_F were not statistically significant at the 95% confidence level. In general, the results indicate that the Freundlich isotherm only adequately describes the adsorption of color from PME onto CFA.

Other researchers have found that the Freundlich isotherm is a fitting model for color adsorption by CFA. Both Prasad and Srivastava (2009) and Andersson et al. (2012) reported that the Freundlich isotherm more accurately described the adsorption system than the Langmuir isotherm.



Fig. 8. Experimental values plotted against values predicted by the linear Freundlich isotherm model. C_i denotes the initial concentration of color in the effluent

	Average Treated PME Sample Measurements					
CFA Dosage (g/L)	рН	Color (mg/L Pt- Co color units)	Color Removal	COD (mg/L)	COD Removal	
0	9.15	928	-	410	-	
100	9.52	534	42.5%	288	29.8%	
150	9.48	383	58.7%	289	29.5%	
200	9.41	252	72.9%	213	48.0%	
250	9.43	162	82.5%	231	43.7%	
300	9.39	102	89.1%	164	60.0%	

Table 6. Effect of CFA dosage on removal of color and COD from PME

3.6. Removal of COD

A limited number of PME samples from the effective dosage batch study were analyzed for COD removal to observe the relationship between this parameter and color removal. Table 6 illustrates that over the CFA dosage range studied, the data shows there was a clear correlation between color removal and COD removal in treated effluent: the higher the dosage of CFA, the higher the color was removed while the higher the COD was also removed from PME. At the previously established effective CFA dosage of 250.0 g/L, over 80% of color and 40% of COD can be removed from PME simultaneously. COD is a widely used wastewater organic strength indicator, especially with regard to organic compounds present in industrial effluent. Therefore, the results of this analysis indicate CFA may be a suitable adsorbent for organic compounds removal from PME.

4. Conclusions

In this research, batch adsorption studies were conducted to determine whether CFA is a suitable adsorbent for cost-effective removal of color from locally-obtained, secondary PME. Overall, the results of this research showed that CFA can be used addition, the optimum adsorption conditions for color removal were determined from batch studies. When the initial effluent color concentration was 900 mg/L Pt-Co color units or lower, the observed effective CFA dosage was 100.0 g/L. For initial effluent color concentrations above 900 mg/L Pt-Co color units, the effective CFA dose was 250.0 g/L. Varying the pH of the PME did not significantly affect color removal. Not altering the initial effluent pH was found to be the most cost-effective condition for color removal from PME. An equilibrium time of 24 hours was established for the adsorption of color by CFA. In addition, it was observed that the bulk of color adsorption (70% percent removal) occurs within the first 1 h of contact. Modeling of the experimental data showed that the Ho and McKay pseudo-second order kinetic model better represents the adsorption kinetics than the Lagergren pseudo-first order model. The Langmuir isotherm was found to best describe the adsorption of color onto CFA at equilibrium, signifying a monolayer coverage of color molecules on the outer surface of the CFA particles. Increases in color removal from PME by CFA were observed to coincide with increased COD removal. The positive relationship between percent removal of color and COD suggests that CFA may be suitable for the removal of other organic compounds from PME.

effectively as a low-cost treatment for PME. In

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