Removal of Organic Pollutants and Decolorization of Bleaching Effluents from Pulp and Paper Mill by Adsorption using Chemically Treated Oil Palm Empty Fruit Bunch Fibers

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Treatment of bleaching effluents from pulp and paper mills using oil palm empty fruit bunch (EFB) fibers as an adsorbent was conducted to remove color and organic pollutants. Empty fruit bunch fibers were chemically modified with polyethylenimine to enhance the adsorption capacity toward anionic species in the effluents. Effluents from the primary clarifier and aerated treatment pond were treated, and the performance of the adsorbent was investigated in terms of decolorization, total organic carbon, and oxygen demand level. Increasing adsorbent dosage and lower pH resulted in greater adsorption performance. The highest decolorization and reduction of total organic carbon of the effluents were 95.0% and 58.2%, respectively. The adsorption equilibrium can be achieved after 4 h of the adsorption process.

Keywords: Decolorization; Kinetics; Low cost adsorbent; Mill effluents; Organic pollutant

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INTRODUCTION

Because of the yearly increase in the demand for paper products, more than 300 million tons of wood are used to produce paper pulp worldwide (Singh *et al.* 2011). This has resulted in a significant increase in pollutants produced from the pulp and paper industry every year. Bleached pulp effluent consist of various lignocellulosic compounds, including degradation products from lignin (2,4-dichloro-phenol, 2,4,6-trichloro-phenol, 3,4,5-trichloro-catechol, 4,5,6-trichloro-guatacol, and tetrachloro-gualacol) (Malik and Grohmann 2012), tannins, cellulose, hemicelluloses, and extractives. Untreated effluent discharged into fresh water increases the level of biological oxygen demand (BOD), chemical oxygen demand (COD), and chlorinated compounds in the water ecosystem. In addition, the use of toxic chemicals in the paper making process, such as resin acids, unsaturated fatty acids, and diterpene alcohol, can be a threat to human health and aquatic ecosystems (Amat *et al.* 2005; Ali and Sreekrishnan 2001; Pokhrel and Viraraghavan 2004). Hence, pulp and paper mill effluent has been highlighted as the sixth largest pollutant in the world (Ali and Sreekrishnan 2001).

Primary clarification is the main treatment process to efficiently remove suspended solids in the pulp and paper industry. The primary treatment is followed by a secondary treatment, *i.e.*, biological treatment (aerobic, anaerobic, or fungal) (Pokhrel and Viraraghavan 2004; Thompson *et al.* 2001). Using microorganisms, biological treatment is a cost-effective method to biodegrade the organic compounds present in the effluent (Singh *et al.* 2008). However, biological treatment has difficulty in removing color from the effluent (Bajpai and Bajpai 1994; Shawwa *et al.* 2001). As a result of oxidation of lignin during the bleaching process, chromophores are the main contributor to the dark brown color of pulp and paper mill effluent. Because of the carbon-carbon biphenyl linkages, these compounds are difficult to degrade using bacteria (Diez *et al.* 1999). The color of effluents can detrimentally affect the productivity of algal and aquatic life, while lignin and its derivatives are toxic to the environment. Therefore, proper treatment is important to decolorize the effluents (Ali and Sreekrishnan 2001; Bajpai and Bajpai 1994).

Adsorption is widely used for the removal of hazardous pollutants from aqueous solution, including heavy metal ions and dyes. It is a less preferred method for the treatment of pulp and paper mill effluent due to the high cost of the initial installation of the treatment system and the lack of a high-efficiency adsorbent, especially for those pulp and paper mills in developing countries (Jain *et al.* 2009; Andersson *et al.* 2012). Nevertheless, an alternative tertiary treatment method, such as adsorption, after the biological treatment, may become important in the future due to more stringent regulation and monitoring of wastewater effluents (Mishra *et al.* 2010; Thompson *et al.* 2001). By considering the high impact of color generated from the industry on water resources, the Bureau of Indian Standards (BIS) and the United States Public Health Services (USPHS) have limited the color level of effluents to be below 101 and 10 Pt-Co/hazen units, respectively (Anjaneyulu *et al.* 2005).

Malaysia generates large amounts of agricultural waste from the palm oil industries. This creates a major source of waste materials, *e.g.*, oil palm empty fruit bunch (EFB) (Mohammed *et al.* 2012). Oil palm EFB fibers have recently been used to produce particle boards, medium-density fiberboard, pulp, paper, and composites (Daud and Law 2011; Rozman *et al.* 2004). The EFB fibers have also been used as an adsorbent material for removing dye from aqueous solution. Using chemical approaches, the hydroxyl groups on the EFB fibers can be further tailored to produce cationic and anionic adsorbents (Sajab *et al.* 2013).

In this work, oil palm EFB fibers were chemically modified with cationic polyethylenimine and used for the treatment of paper mill effluents. Because of the negative charge on the organic compounds in the effluent, it is believed that the high density of cationic amine groups present in polyethlenimine will be a viable match (Ali and Sreekrishnan 2001). Two bleaching effluents from different stages of the pulp and paper mill effluent treatment process, *i.e.*, effluent after the primary clarifier and effluent after biological aeration, were collected for this study. After the adsorption process using the modified EFB fibers, the changes in TOC, color, and biochemical oxygen demand (BOD_5) of the effluents were examined.

EXPERIMENTAL

Preparation of Chemical Modification of EFB Fibers

Oil palm EFB fibers were prepared and modified according to our previous study (Sajab *et al.* 2013). In addition to a brief NaOH washing, the EFB fibers underwent chemical modification using polyethyleneimine (PEI) (MW ~750,000, 50 wt. % in H_2O) with a ratio of 100 g/L of the EFB fibers in solutions of 5% PEI (w/v). The fibers were further treated with glutaraldehyde (1% v/v) as a crosslinker. The modified EFB fibers were then washed several times to completely remove excess chemicals, dried in an oven at 60 °C, and kept in a desiccator for further use. The surface charge of the raw and treated EFB fibers was examined using a Malvern Zetasizer Nano ZS.

Pulp and Paper Mill Effluent

Bleaching effluent was collected from one of the paper mills in Eastern Finland. Effluents collected after passing the primary clarifier and biological aeration were labeled as Effluent A and Effluent B, respectively. The collected effluent was refrigerated at 4 °C until further use. Standard methods for BOD_5 and COD characterization were followed (APHA 1998). The effluents' color unit was measured according to the Platinum-Cobalt method using a UV-Vis spectrophotometer (Lange DR 2800). The TOC of the effluents was measured using a TOC analyzer (Shimadzu 5000 A).

Adsorption Studies

Adsorption experiments were carried out using various adsorbent dosages (0.1, 0.3, 0.6, and 0.9 g) and pH (3, 5, 7, and 9) in a 100-mL vial. The vials were placed in a water bath shaker with a constant speed of 200 rpm at a controlled temperature for 24 h. The BOD_5, TOC, and color of the effluents after the adsorption process were measured. The color and TOC at equilibrium (C_e) was measured and used to calculate the total adsorption of color and TOC at equilibrium (q_e) using the following equation,

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of TOC (mg/L) and color (Pt-Co), respectively. The quantity V is the volume of the solution (mL), and m is the mass of adsorbent (g).

The adsorption kinetics was investigated in a flask containing 300 mL of effluent and 1.8 g of EFB fibers. The mixture was stirred at a constant speed of 250 rpm with a magnetic stirrer for 8 h until reaching equilibrium. During the adsorption, aliquots of solution (~2 mL) were taken at various intervals, centrifuged, and measured to determine the TOC and color of the effluent. The reduction of TOC and color of the effluent at time t, q_t (mg/g), was calculated using following equation,

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

where C_t stands for the concentrations of TOC (mg/L) and color (Pt-Co) at time t.

Preliminary adsorption experiments of Effluent A and Effluent B were carried out using the untreated EFB fibers. The results indicate that there were no obvious changes on color and TOC of both effluents after the adsorption process.

RESULTS AND DISCUSSION

Effluent Characterization

The characteristics of Effluent A and Effluent B are presented in Table 1. The primary treatment is mostly to remove suspended solids from the bleaching effluent of pulp and paper mills. To further reduce the BOD and COD, the effluent underwent aerated treatment (Jain *et al.* 2009).

As seen in Table 1, the COD, BOD_5, TOC, and AOX of Effluent B were significantly reduced after the aeration treatment. However, only a 55.5% color reduction was achieved, revealing the difficulty in degrading lignin and its derivatives during biological aeration treatment (Ali and Sreekrishnan 2001; Pokhrel and Viraraghavan 2004).

Table 1. Characteristics of Effluent A and Effluent B

Parameter	Effluent A (*after primary clarifier*)	Effluent B (*after aeration treatment*)
pH	7.3	8.5
COD (mg/L)	1500*	122*
BOD_5 (mg/L)	240	148
TOC (mg/L)	445	121
AOX (mg/L)	8.9*	−
Color (Pt-Co)	963	429
Total suspended solid (mg/L)	450*	87*
P total (µg/L)	540*	−
Na total (mg/L)	800*	−
N total (mg/L)	5.6*	−
*: Provided by the pulp and paper mill −: Not analyzed		

Effect of Adsorbent Dosage

Figure 1 shows the effect of adsorbent dosage on the reduction of color, BOD_5, and TOC of the effluents. Increasing adsorbent dosage led to a significant reduction in the color and BOD of both Effluent A and Effluent B. Using 9 g/L of adsorbent, BOD_5 was reduced by approximately 32.3% and 90.4% in Effluents A and B, respectively. The highest decolorization for Effluents A and B was 93.6% and 87.5%, respectively. This is further supported by the images shown in Fig. 2. In comparison with a previous study, the decolorization performance of the EFB fibers is comparable to that of polymer resin (polystyrene divinylbenzene copolymer) and much better than that of activated carbon (Srivastava *et al.* 2005).

However, only a slight reduction in the TOC can be observed with increasing adsorbent dosage. It is believed that larger compounds with lignin and tannin are more easily removed by adsorption, as compared to smaller compounds, which contribute more to the TOC in effluent (Zhang and Chuang 2001). The decrease in the effluent color, associated with the decrease in BOD_5, can be explained by the removal of oxidized compounds of lignin and tannin, which would also contribute to the BOD_5 of the effluent.

In addition, the results suggest that the adsorption using PEI-modified EFB fibers is comparable to the aerated treatment practiced in the pulp and paper mill on effluent after the primary clarifier process. Approximately 3 g/L of EFB fibers are required to treat Effluent A to achieve the same color level of Effluent B treated using aerated treatment (450.6 and 429.4 Pt-Co units, respectively). However, the reduction in TOC was much lower than that achieved with aeration treatment.

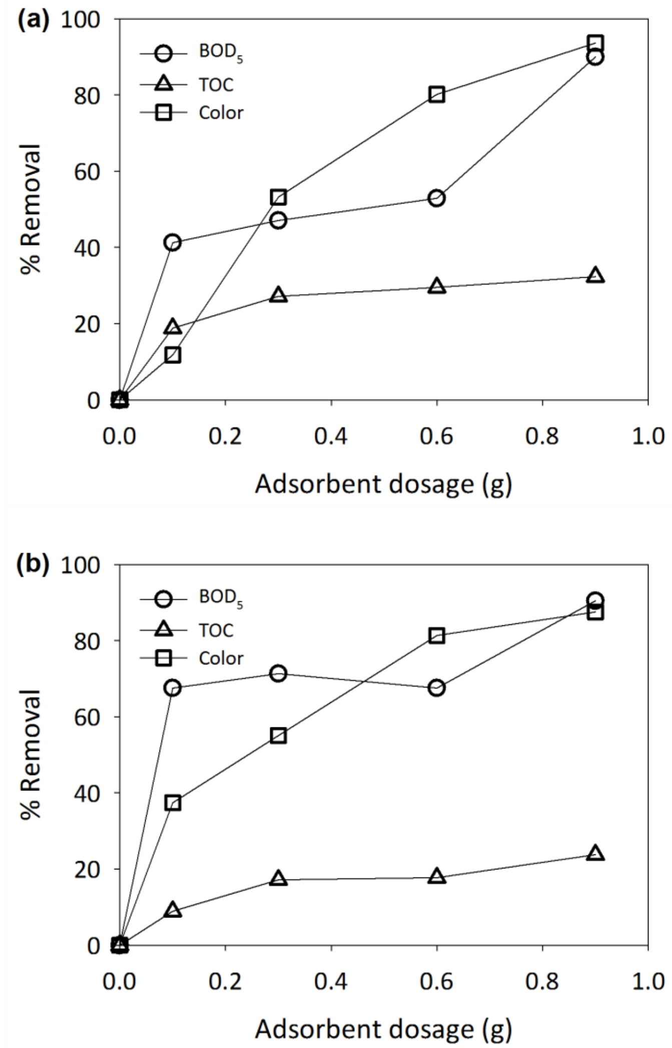

Fig. 1. Adsorption diagram for removal of TOC, color, and BOD_5 of (a) Effluent A and (b) Effluent B using different modified EFB adsorbent dosages: 1 to 9 g/L

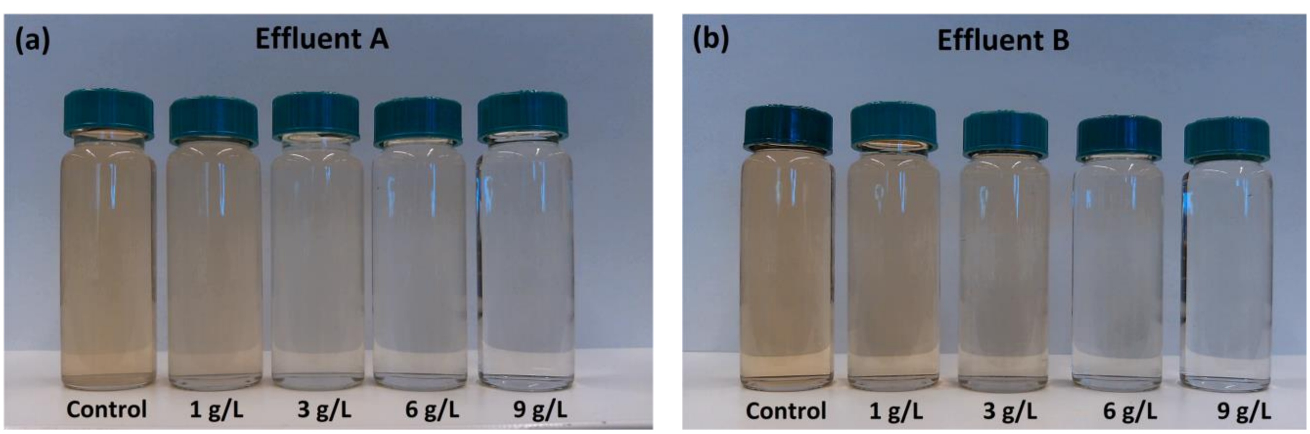

Fig. 2. Decolorization of (a) Effluent A and (b) Effluent B using different modified EFB adsorbent dosages: 1 to 9 g/L

Effect of pH

The removal of TOC and color of the effluent was higher at lower pH. The cationic surface charge of the modified EFB fibers is higher at lower pH and thus enhanced the adsorption performance toward negatively charged acidic lignin compounds (Ali and Sreekrishnan 2001; Amat *et al.* 2005; Sajab *et al*. 2013). Additionally, it is believed that, at lower pH, there is less competition between the adsorbate molecules and hydroxyl ions (Anirudhan and Ramachandran 2006; Mohan and Karthikeyan 1997; Srivastava *et al.* 2005; Ugurlu *et al.* 2005).

The higher zeta potential of the treated EFB fibers could also be one of the reasons for the greater adsorption (Fig. 3). TOC reductions of 43.1% and 58.2% for Effluents A and B, respectively, were achieved at pH 3 (Fig. 3). Meanwhile, at the same pH, there was more than 95% decolorization for both effluents.

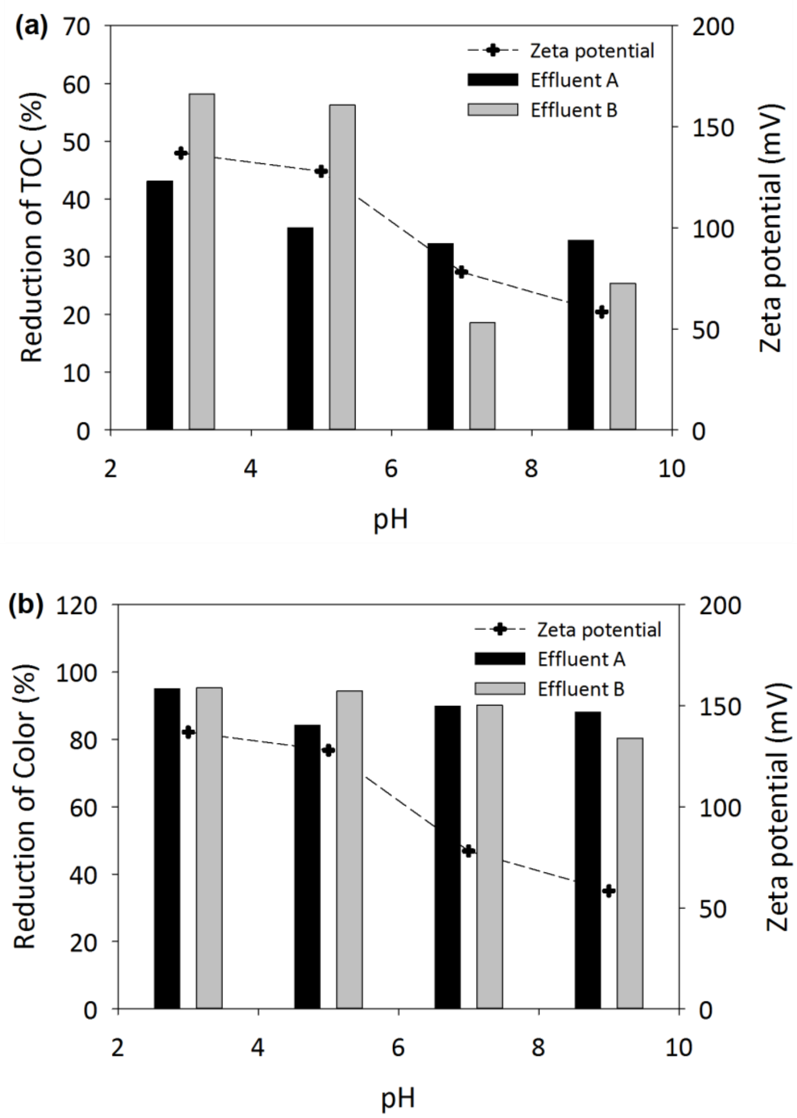

Fig. 3. Influence of pH of Effluents A and B on removal of (a) TOC and (b) color and correlation with zeta potential of modified EFB fibers (adsorbent dosage: 6 g/L; pH 3 to 9)

Adsorption Kinetics

The adsorption data were fitted with the pseudo-second order and intraparticle diffusion models as follows:

The equation for the pseudo-second order kinetics model (Ho and McKay 1999) is,

$$q_t = \frac{k q_e^2 t}{1 + k q_e t} \tag{3}$$

where k is the pseudo-second order rate constant.

The adsorption kinetics data for TOC and color were well fitted to the pseudo-second order model, as suggested by the high coefficient of determination r^2 ~0.95 (see Fig. 4). The TOC reduction of Effluents A and B were 27.5% and 32.1%, respectively. The adsorption rates (k) of TOC for Effluents A and B are 2.77×10^{-3} and 1.32×10^{-3} g/mg min, respectively.

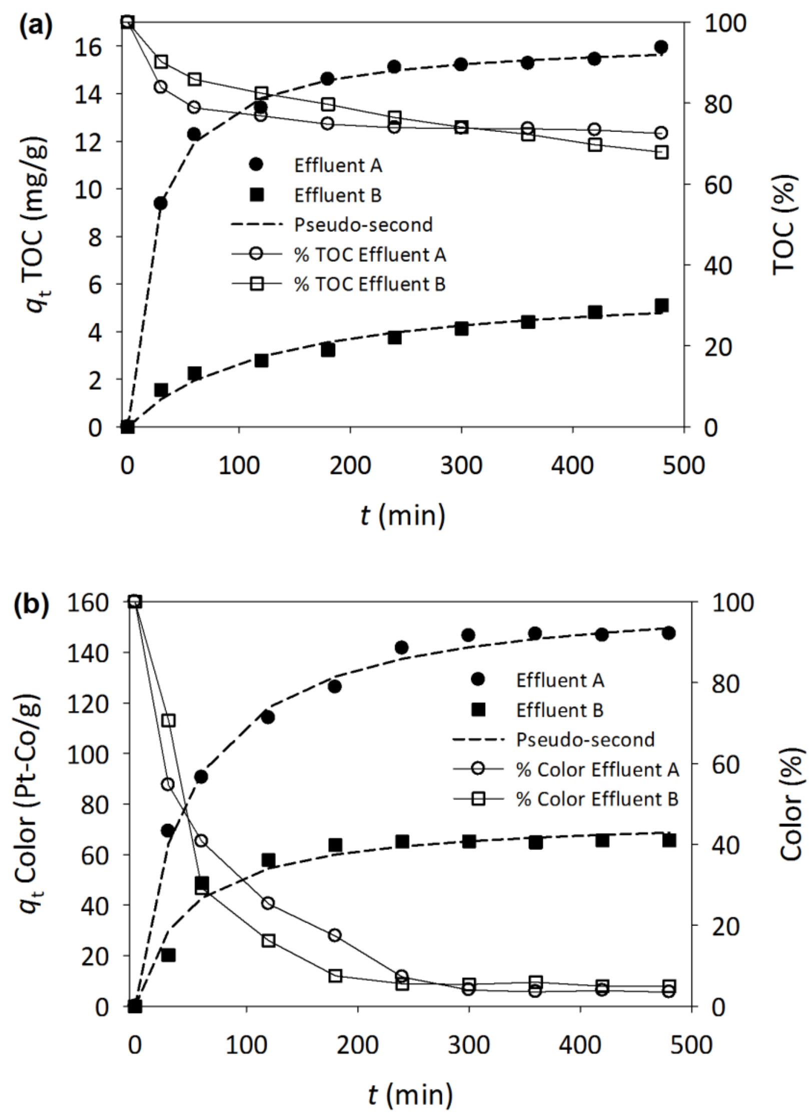

Fig. 4. Adsorption kinetics of Effluents A and B for (a) TOC and (b) color removal onto EFB fibers fitted with a pseudo-second order model (adsorbent dosage: 6 g/L; pH 3)

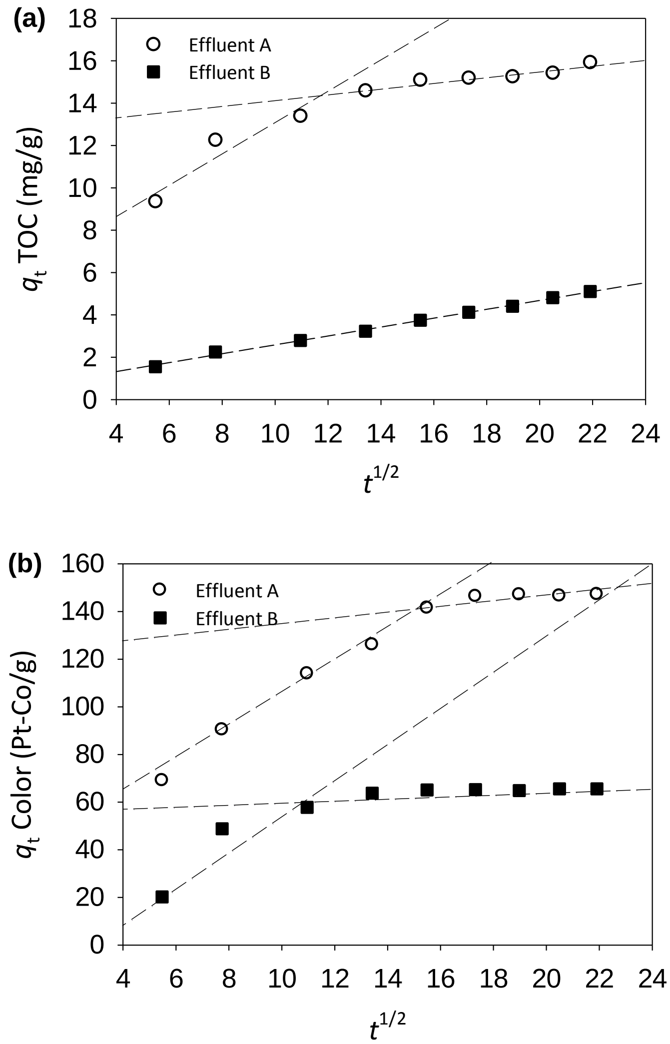

Fig. 5. Adsorption kinetics of Effluents A and B for (a) TOC and (b) color removal using EFB fibers fitted with an intraparticle diffusion model (adsorbent dosage: 6 g/L; pH 3)

The higher *k* value for the TOC adsorption from Effluent A may be due to the higher initial TOC content, as the result of the higher content of high-molecular weight lignin and tannin compared to Effluent B (Ali and Sreekrishnan 2001; Srivastava *et al.* 2005). The better performance of the adsorbent in removing color from both effluents as compared to the removal of TOC, can be observed in Fig. 4b. The removal of color for Effluents A and B were 96.5% and 95.0%, respectively, after 4 h of adsorption.

To investigate the adsorption behavior of TOC and color on the adsorbent, the intraparticle diffusion model was used to interpret the adsorption kinetics data (Weber and Morris 1963),

$$q_t = k_i t^{1/2} + C \qquad (4)$$

where k_i is the intraparticle diffusion constant and C is the constant for any experiment (mg/L) as the slope of a plot of q^t against $t^{1/2}$. The plots for the adsorption of TOC from Effluents A and B are distinct from each other (see Fig. 5). For Effluent A, two linear sections of the fitting can be observed, suggesting that adsorption of TOC from Effluent A involves two steps: surface mass transfer and intraparticle diffusion (Wu *et al.* 2009). For Effluent B, only a single linear section can be observed, which reveals that the adsorption of TOC from Effluent B does not involve intraparticle diffusion due to a lower initial TOC content.

Two linear sections of the intraparticle diffusion plots for the adsorption of color from both Effluents A and B can be observed in Fig. 5b. The rate of adsorption of the large lignin and tannin compounds may have been limited by the diffusion step to move to the inner pores of the adsorbent.

CONCLUSIONS

1. Modified, low-cost EFB fibers are a viable alternative adsorbent treatment for pulp and paper mill bleaching effluent.

2. Decolorization as high as 95% in Effluent A was achieved by adsorption using the modified EFB fibers. Compared to aeration treatment, with only 55.5% decolorization, this is much higher.

3. After going through the adsorption process using the modified EFB fibers, the color level of both effluents met the BIS regulation.

4. The modified EFB fibers can be a potential adsorbent for effluent from primary clarifier or secondary aeration treatments. In addition, the fibers can be introduced for a tertiary adsorption treatment in pulp and paper mills to improve the quality of discharged effluent.

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