



## Developing performance-property correlation for fly ash as adsorbent for pulping effluents

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### ABSTRACT

Wood based fly ash has a limited use in industry currently, but it can be used as an adsorbent in wastewater treatment systems. In this work, physical (e.g., surface area, pore size) and chemical (e.g., compositions) properties of fly ash were investigated and related to its performance in removing lignocelluloses from a pulping spent liquor (SL). To achieve this goal, two different industrially produced wood-based fly ash (FA) samples, FA1 and FA2, were used. The results revealed that the removals of COD, lignin and turbidity were 80%, 95% and 96% for FA1 and 30%, 25% and 50% for FA2, respectively, under the experimental conditions of 100 g/L dosage at 25 °C for 1 h. The heating value of fly ash was also increased after adsorbing the organic compounds. To investigate the impact of inorganic components, fly ash samples were incinerated at 525 and 900 °C, and then they were used for removing organic materials. The analysis depicted that the removals were limited when incinerated FA1 was used, while incinerated FA2 at 900 °C had more organics removal than FA2. Overall, it was concluded that even though the physical properties of fly ash impacted the adsorption of organics, the chemical compositions of fly ash played a more crucial role on its performance in removing lignocelluloses.

### 1. Introduction

Adsorption is one of the most commonly used methods for removing contaminants from waste streams. Its simplicity in design, ease of operation, facile regeneration of adsorbent and comparatively low operation costs make it one of the most feasible processes used in industry for waste management [1]. Activated carbon (AC) is known as an effective adsorbent for removing organic pollutants from wastewater [2]. However, the relatively high price of activated carbon has hampered its attractiveness for industrial use [3]. Hence, more cost effective adsorbents are required for adsorption processes.

Fly ash is a solid waste with a large surface area, many active sites and with a strong adsorption capacity, which has a relatively low price [4]. In the past, fly ash was investigated as an adsorbent for removing contaminants such as dyes [5], dairy wastes [6], lignin, and extractives [7] from different wastewater effluents. In these studies, the adsorption of organic compounds on fly ash was affected by physical (i.e., surface area, pore size and pore volume) and chemical properties. The removals of organic materials from wastewaters can also be associated with three phenomena on the surfaces of fly ash, 1) attraction between resonating  $\pi$ -electrons of carbon on the aromatic ring of adsorbents and the protons located on the surface of fly ash [8], 2) interaction of anionic

groups such as carboxylate, lactone, and phenol of the adsorbents [9] and the cationic group (such as amide, imide and lactam) located on the surface of fly ash [10], and 3) the interaction between metal compounds, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Ca}(\text{OH})_2$  of fly ash and the anionic charged groups of adsorbents present in wastewater effluents [11]. The removal of dyes from aqueous solutions using fly ash was based on physical adsorption [12]. When the surface area and pore volume of fly ash increased from 2.5  $\text{m}^2/\text{g}$  to 276  $\text{m}^2/\text{g}$  and from 0.005  $\text{mL}/\text{g}$  to 0.022  $\text{mL}/\text{g}$ , respectively, the adsorption of dye improved from 0.014  $\text{mmol}/\text{g}$  to 0.025  $\text{mmol}/\text{g}$  under the treatment conditions of 1 g/L fly ash dosage in the dye solution at pH 5.2 and 30 °C for 72 h [12]. In another study, bagasse fly ash and activated carbon were used for removing congo red from an aqueous solution [13]. The removal of congo red was 99.4% and 30.1% after the treatment of bagasse fly ash and activated carbon, respectively, at 1 g/L dosage and 30 °C for 4 h, while the surface area of bagasse fly ash was 168  $\text{m}^2/\text{g}$  and that of the activated carbon was 492  $\text{m}^2/\text{g}$  [13]. In this case, the physical properties played a minor role, whereas the chemical compositions played a crucial role in the removal as fly ash contained 26.43% inorganics such as  $\text{Al}_2\text{O}_3$  and CaO, but the activated carbon did not contain inorganic materials [13]. Alonso-Davila reported that the removal of pyridine from an aqueous solution by fly ash was attributed

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to the electrostatic interactions between  $\pi$  electrons of graphene layers in baggage fly ash and metal oxides of fly ash [8].

In our previous study, the optimization of fly ash as an adsorbent for treating the spent liquor (SL) of a thermomechanical pulping (TMP) process led to 89%, 49% and 53% removals of turbidity, COD, and lignin, respectively, under the conditions of 110 g/L dosage at 30 °C for 3 h [14]. In another study, it was discovered that the maximum COD (91.3%) and lignin (95%) removals from the SL of a TMP process were achieved by using fly ash with a particle size of 0.43 mm at a dosage of 70 g/L and a particle size of 0.11 mm at a dosage of 46.5 g/L, respectively [15]. In addition, our previous studies showed effective separation of the fly ash from treated wastewater by sedimentation and filtration, which enhanced the feasibility of fly ash adsorption treatment in practical implementation [16]. However, it is still unclear how the properties of fly ash affect the removals of organics from the SL. The contribution of physical structure and chemical characteristics of fly ash to the adsorption process have not been studied. The fundamental interactions between fly ash and organic materials in the SL should be discovered to identify the mechanism for the removal of organics from SL by fly ash. The main novelty of this work is the developed correlation between the properties and performance of fly ash as an adsorbent for removing organics from the SL of a TMP process. Incineration of fly ash at 525 and 900 °C was investigated to reduce or eliminate the effect of physical adsorption of lignocelluloses on fly ash. Incineration of fly ash would also offer studies on the recyclability of fly ash for removing lignocelluloses from wastewater.

## 2. Methodology

### 2.1. Materials

Two different types of fly ash (FA1 and FA2) were collected from a bark boiler of a pulp mill in Northern Ontario, Canada biweekly for one year. The fly ash samples were stored in a dry and ventilated location prior to use. It should be stated that the properties of FA samples were tested biweekly and the relationship developed in this work is based on the average values over 1 year of experimentation. TMP spent liquor (SL) was produced from the same mill via hot water treatment of hardwood chips at 80 °C for 1 h prior to refining for TMP pulp production. The SL was maintained in a 4 °C fridge prior to use. Polydiallyldimethylammonium chloride (PDADMAC) with a molecular weight of 100–200 kg/mol (20 wt.% solution) as well as sodium hydroxide and potassium chloride (analytical grades) were purchased from Sigma-aldrich. Polyvinylsulfate potassium (PVSK) with a molecular weight of 100–200 kg/mol (98.4% esterified) was provided by Wako Pure Chem. Ltd., Tokyo, Japan. Sulfuric acid was purchased from Caledon Laboratory Chemicals Company. The chemical oxygen demand (COD) kit, K-7365 (0–1500 mg/L), was purchased from CHEMetrics Inc.

### 2.2. Thermal treatment of fly ash

Fly ash was combusted to eliminate its organic portion in order to produce organic free fly ash samples (FA1 525 and FA2 525) via incinerating in a muffle furnace at 525 °C for 5 h following Tappi T 211 om-02. In another set of experiments, fly ash samples were incinerated at 900 °C for 5 h to prepare fly ash samples without carbonate and sulphate contents (FA1 900 and FA2 900) according to Tappi T413 om-93. The samples were collected when the weight of fly ash samples in the furnace was no longer changed as time elapsed.

### 2.3. Treatment of spent liquor with fly ash

In this set of experiments, different dosages of the fly ash samples were added to the SL (dosage of 20–120 g/L FA/SL). The mixtures were incubated in a water bath shaker at 25 °C and 100 rpm for 60 min. The control samples without fly ash treatment were prepared under the

**Table 1**  
Properties of SL.

COD, g/L	Lignin, g/L	Turbidity, NTU	Sugar, g/L	pH
2.33 ± 0.25	1.07 ± 0.06	262 ± 88	0.493 ± 0.01	5.55 ± 0.37

same experimental conditions. Subsequently, all suspensions were filtered using Whatman filters (NO. 1) and the filtrates were then collected for COD, turbidity, lignin, and sugar concentration analyses.

### 2.4. Structural analysis of FA

The macrostructure of fly ash was evaluated using a Hitachi SU-70 scanning electron microscope (SEM) at 10 kV under  $10^{-4}$ – $10^{-3}$  Pa. Two different amplifications ( $\times 50$  and  $\times 1000$ ) were chosen to observe the morphology of fly ash.

Surface area, pore size, and pore volume of fly ash samples were detected by NOVA-2200e Autosorb (Quantachrome Instruments, USA). Fly ash samples were pretreated at 105 °C in an oven overnight for moisture removal [14] prior to the measurement. In this set of experiments, 0.05 g (o.d.) of fly ash was degassed for 3 h at 150 °C using N<sub>2</sub> as the carrier gas prior to analysis. The surface area of the fly ash was calculated according to the multilayer adsorption isotherm derived by NovaWin software (Quantachrome Instruments, USA) in a relative pressure range  $p/p^0$  of 0.05–0.3 [17]. Pore size and pore volume were analyzed following density functional theory method (DFT) via the NovaWin software (Quantachrome Instruments, USA).

### 2.5. Heating value analysis

The heating value of fly ash was measured by burning fly ash samples in a Parr 6200 oxygen bomb calorimeter (Parr instrument company, USA) under controlled conditions according to ASTM E 711-87 (2004). In this method, 0.8–1.2 g of samples were placed in the specimen containers and then loaded onto a calorimeter chamber with oxygen supply. The heating value was analyzed after sample combustion.

### 2.6. Charge density and zeta potential analyses

A particle charge detector (Mütek PCD 04, Germany) with the standard solutions (5 mM) of PVSK and PDADMAC were used for analyzing the surface charge density of fly ash following a back titration method [18]. In this method, 4 g of fly ash samples were mixed with 20 mL solutions of PDADMAC or PVSK for 12 h at room temperature. Then, fly ash was filtered and the supernatants were collected and titrated using a PCD titrator. The surface charge density of the fly ash was calculated based on the concentration difference of PDADMAC or PVSK in supernatants and in their corresponding control samples [19].

The zeta potentials of SL before and after treating with fly ash samples were measured using a zeta potential analyzer, ZetaPALS, Brookhaven Instruments Co., USA. In this study, 1 mL of SL before and after treating with the fly ash samples was added to 20 mL of KCl solution (1 mM) and then the zeta potentials of the samples were measured.

### 2.7. Metal and organic element analysis

To determine the metal contents of the samples, they were mixed with a mixture of nitric acid and hydrochloric acid (1/3 mol/mol) according to EPA method 3051a, and then digested in a microwave oven (CEM Mars xpress, USA) via heating from room temperature to 175 °C for 20 min and then maintained the temperature at 175 °C for 25 min. Afterward, the digested samples were diluted to 40 mL with distilled water and then the elements contained in the samples were analyzed by

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