INVESTIGATING THE REMOVAL OF METHYL TERTIARY BUTYL ETHER (MTBE) FROM WATER USING RAW AND MODIFIED FLY ASH WASTE MATERIALS

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ABSTRACT

There are a number of classical remediation techniques that have been tested for the removal of methyl tertiary butyl ether (MTBE) from contaminated water source such as air stripping, adsorption by activated carbon (AC), bio-treatment and chemical oxidation. However, each remediation technique is characterized by inherent limitations due to the special physical and chemical characteristics of this compound, making further researches on MTBE remediation promising. Fly ash (FA), which is a waste material derived from the combustion of coal or heavy liquid fuel has been reported to show favourable results in its application for adsorption of selected heavy metals, dyes and some organics in aqueous solution. In this study, raw FA, acid treated FA and metal oxide (silver, iron and aluminium) impregnated FA were assessed on a bench scale, for their adsorption efficiencies for MTBE treatment in contaminated water system and benchmarked against AC. Results revealed that only silver oxide (Ag_2O) impregnated FA showed about 24% removal of MTBE in aqueous solution, while the other tested adsorbent materials showed less than 10%. MTBE optimum adsorption was attained after 120 min of contact, and 50mg dosage of adsorbent. On the other hand, results showed that silver oxide impregnation of AC brought about a drop in the MTBE removal efficiency of AC from an optimum MTBE removal efficiency of 71% to 53%. Also, the Langmuir isotherm model best represented the MTBE adsorption behaviour of both the Ag_2O impregnated FA and AC, having R^2 of 88.75% and 89.92% respectively.

Keywords: MTBE, Adsorption, Fly ash, Metal oxides, Optimum adsorption

1. Introduction

Methyl tertiary butyl ether (MTBE) is an established contaminant of water sources, primarily used as gasoline oxygenate, in replacement of tetra-ethyl lead. Leakage from underground storage tanks and accidental spills are its major routes for environmental contamination. Its high solubility (50,000 mg/L), low organic-carbon partition coefficient K_{oc} (11 mg/L) and poor natural degradation make it persistent in the environment (Squillance *et al.,* 1996). The unpleasant odour and taste of contaminated system are primary concerns associated with MTBE. Also, the US Environmental Protection Agency considers MTBE to be a potential human carcinogen, with advisory level for MTBE ranging from 20 to 40 µg/L (USEPA, 1997b).

Remediation technologies such as adsorption, air stripping, and oxidation treatment have recorded varying levels of success with MTBE. However, each is characterized by inherent limitations, which create the opportunity for further research. Granular activated carbon has recorded significant success in removal of MTBE from aqueous solution, hence regarded as the established adsorbent of MTBE (Sutherland *et al.,* 2004). Studies on the use of readily available low cost materials for the removal of environmental contaminants are considered viable alternatives.

Fly ash (FA) constitutes the major particulate waste by-product from burning of coal or heavy liquid fuel. Generated as a non-combustible, fine residue, carried in the flue gas and usually collected with the aid of electrostatic precipitators, and having a uniform size distribution of particles ranging 1 to 10 μm. Presently, the major applications of FA are in soil stabilization and as additives in the manufacturing of cements, with a large proportion of the FA material being disposed by land filling (Mott and Weber, 1992).

Application of FA as adsorbent for contamination treatment is considered an alternative form of waste management. The potential of raw FA and metal oxide modified forms to remove MTBE from contaminated water system was the primary focus of this work. Effects of experimental conditions such as adsorbent dosage and contact time on the adsorption efficiency were also considered to determine the optimum condition for treatment using FA. Performance of the FA based materials was then benchmarked against AC, in order to better understand their adsorption mechanisms.

2. Materials and Methods
2.1. Chemicals
The MTBE used in this study was purchased from Sigma-Aldrich, Saudi Arabia, with 99.999% purity (HPLC grade). Aluminium nitrate [$Al(NO_3)_3.9H_2O$], ferric nitrate [$Fe(NO_3). 9H_2O$] and silver nitrate ($AgNO_3$) used as sources of aluminium, iron and silver respectively were locally. Deionized water from Milli-Q direct purification system was used for preparation of the aqueous solutions, with MTBE stock solutions prepared by appropriate dilutions. A stock standard solution of 100 mg/L of MTBE was prepared.

2.2. Preparation of Raw and Modified Fly Ash Materials
The raw FA was treated with nitric acid in the volume ratio of 1:3 (ash: nitric acid). The mixture was stirred for 24hrs at 120°C, with an attached condenser. Segregation of phases was ensured by allowing the mixture to stand for 2hrs, after which the acid was decanted and the slurry phase was washed with deionized water. Subsequently, the slurry phase was oven dried at 100°C for 24hrs and stored until used for the batch experiments.

For the modified FA, a 10% (by mass) metal oxide impregnation was carried out using aluminium nitrate [$Al (NO_3)_3.9H_2O$], ferric nitrate [$Fe (NO_3). 9H_2O$] and silver nitrate ($AgNO_3$) as sources of aluminium, iron and silver respectively. For each adsorbent material, 90% FA of total mass was added and soaked in ethanol, then sonication of mixture for 30mins, calcination at 350°C for 3hrs and the resultant material stored until used for batch adsorption experiment. The granular AC used for comparison was purchased from a local supplier and similarly subjected to 10% impregnation with silver oxide.

2.3. Adsorption Runs
Each batch experiment was carried out in a 125 mL conical flask with a Parafilm sealing membrane. 100 mL MTBE solution of 1000 μg/L initial concentration was used. Blank experiments were conducted to assess the loss of MTBE to the flask and environment during the sorption process. Seven (7) different forms of adsorbent materials (namely; raw FA, acid treated FA, three forms of metal oxide impregnated FA, AC alone and silver oxide impregnated AC) were used in the study. Dosages of the adsorbent materials, ranging from 10mg to 100mg were used for the sorption tests and contact time from 30min to 300min. Duplicate 1.0 mL water samples were collected at 60min interval in a glass vial and analyzed for MTBE concentration using GC/MS system.

2.4. Analysis Method
The MTBE concentration in the aqueous solution was determined using a gas chromatography coupled with ISQ single quadrupole mass spectrometer system, fitted with a Triplus headspace injector unit and an auto-sampler. A 60m x 0.32mm x 1.80μm Rxi-5ms fused silica capillary column was used with helium as carrier at 1.7mL/min flow rate. Selected ion monitoring (SIM) mass spectrometer (MS) mode was set at a mass range at 72.50 – 73.50 for MTBE.

3. Results and discussions

3.1. Characterization of the Fly Ash by SEM/EDXS

A Scanning electron microscopy (SEM) equipped with energy dispersive X-Ray (EDXS) was used to characterize the FA and study its surface morphology. The micro-chemical analysis of raw FA material for an area with a representative amount of the adsorbent material showed the adsorbent to be mainly composed of carbon, with considerable amount of oxygen. From the SEM micrographs (Fig. 1), the orbicular structure of the FA powder can be observed, having approximately 100 µm average grain diameter and heterogeneous pores.
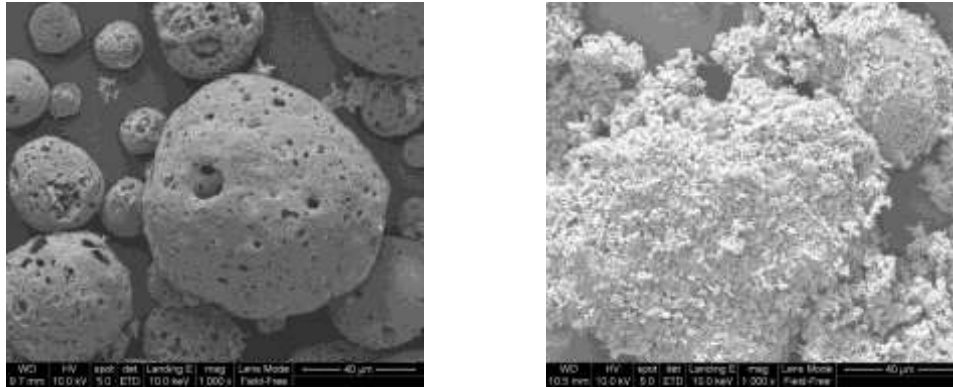
Figure 1: SEM micrographs of raw fly ash (left) and modified fly ash, Ag_2O-FA (right)

3.2. Effects of Experimental Variables on MTBE Removal

3.2.1. Effect of Contact Time on MTBE Removal Efficiency

Adsorption time requirement for most studies vary based on the nature of interaction occurring between the adsorbent and solution. Fig. 2 shows increase in MTBE adsorption with time for all adsorbents across the different dosages tested and an optimum adsorption reached at 120 min, beyond which no significant improvement in MTBE removal was observed. The slight drop in MTBE adsorption observed beyond 180 min can be attributed to saturation of active sites on the adsorbents and a point at which desorption rate was slightly above adsorption rate (Li *et al.,* 2012). The comparative study with AC also showed increase in MTBE removal with time and an optimum removal at 120 min. The results from both FA and AC established that the optimum contact time for MTBE adsorption in this study was 120 min.

3.2.2. Effect of Adsorbent Dosage on MTBE Removal Efficiency

Adsorbent dosage affects removal efficiency due to its influence on adsorption capacity, based on the number of active adsorption sites available (Etim *et al.,* 2012). Only silver oxide impregnated FA (Ag-FA) showed material adsorption of MTBE, while other FA based adsorbents could not achieve removal beyond 10% as shown in Fig 3. Ag-FA showed increase in MTBE adsorption with increase in dosage, and a peak adsorption of 24% with 50 mg, beyond which a slight decrease in adsorption was observed. The availability of more adsorption sites due to increase in adsorption surface area can be presumed responsible for the increase in MTBE adsorption with increase in adsorbent dosage. The decline in adsorption beyond optimum dosage of 50 mg can be attributed to overlapping or aggregation of adsorption sites resulting in surface area reduction (SenthilKumar *et al.,* 2010). Also, comparative study with AC showed increase in MTBE adsorption with dosage increase and a peak adsorption of 71% with 100 mg under same experimental setup as used for the FA materials.

3.2.3. Effect of Silver Oxide Impregnation on MTBE Removal Efficiency

Different adsorption studies have shown that modification of porous materials using metal oxides was able to enhance their adsorption efficiency. In this study, only silver oxide impregnated FA showed notable improvement in its removal of MTBE from the aqueous solution. Hence, to better understand its role on FA for MTBE removal, AC was impregnated with silver oxide and used for similar bench scale water treatment. Fig. 4 shows an increase from <10% to 24%, while a

decrease from 71% to 53% for AC following silver oxide impregnation. The Brunner Emmett Teller surface area analysis of these materials also showed an increase from 7154 m^2/g to 16789 m^2/g and a decrease from 1126.631 m^2/g to 1039.4770 m^2/g for FA and AC respectively. These observations prompted an assumption that the improvement in MTBE removal by Ag-FA was driving by the increase in surface area and number of active sites.

### 3.3. Combination of Activated Carbon and Fly Ash Based Materials

To understand the potential for synergistic removal of MTBE from aqueous solution, 50 mg (1:1) mixtures of different FA based materials and AC were tested and benchmarked with MTBE removal by 50 mg AC alone. Mixtures of AC with both raw-FA and Fe-FA adsorbed less than equivalent dosage of AC alone, while mixture of AC and Ag-FA was able to match the MTBE adsorption using equivalent dosage of AC alone, as shown in Fig. 5. This observation is important from a waste management point of view, where consideration is not limited to cost of impregnation, but also cost of FA disposal. Hence, AG-FA could be used to reduce the amount of AC in a treatment process.
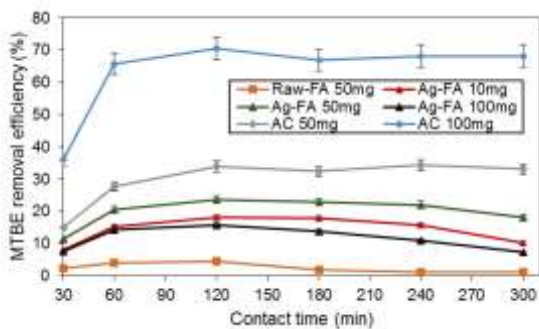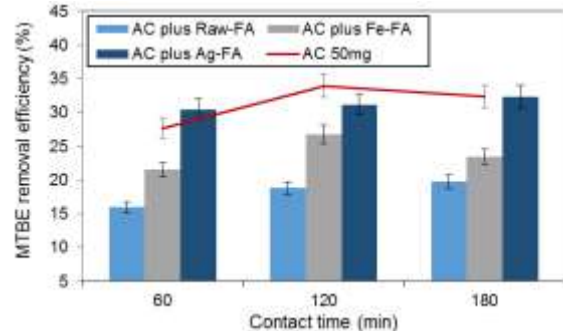

Figure 2: Effect of contact time on MTBE adsorption behaviour of FA based adsorbents and AC at room temperature, 200rpm, 100 mL, pH 6 and 1000 µg/L initial MTBE concentration
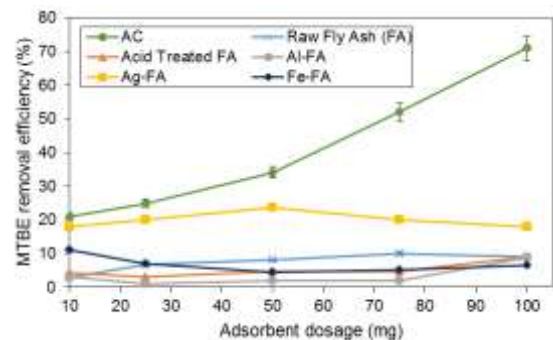
Figure 3: Effect of adsorbent dosages (mg) on MTBE adsorption behaviour of different FA materials and AC at room temperature, 200rpm, 100 mL, pH 6, 120 min and 1000 µg/L initial MTBE concentration
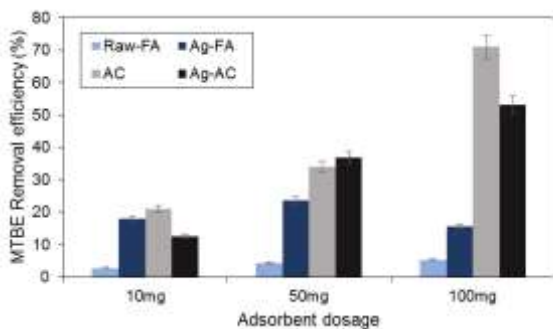
Figure 4: Effect of silver oxide impregnation of fly ash and activated carbon on their MTBE adsorption at room temperature, 200rpm, 100 mL, pH 6 and 1000 µg/L initial MTBE concentration

Figure 5: Comparison of MTBE removal efficiency of 50mg AC alone with 50mg (1:1) mixtures of AC and FA based materials at room temperature, 200rpm, 100 mL, pH 6 and 1000 µg/L initial MTBE concentration

3.4 Adsorption Isotherms Study

Langmuir and Freundlich isotherms were used to assess the MTBE adsorption behaviour of the silver oxide impregnated FA in this study. Langmuir (1916) isotherm model, which explains monolayer adsorption, was found to better represent the data obtained in this study, for both Ag-FA and AC, having higher r-square values. Table 1 summarizes the isotherms parameters calculated from optimum adsorption of MTBE onto Ag-FA and AC.

Table 1: Isotherm parameters from optimum adsorption of MTBE onto silver oxide impregnated fly ash and activated carbon

	Langmuir Model					
	Equation	Slope	R^2	Intercept	q_{max} (mg/L)	K_L (L/mg)
Ag-FA	y = 13.35x - 16.65	13.35	0.8875	-16.65	0.060	1.2472
AC alone	y = 2.881x - 2.3385	2.881	0.8992	-2.3385	0.428	0.8118
	Freundlich Model					
	Equation	Slope	R^2	Intercept	K_F (mg/g)	n
Ag-FA	y = 0.0561x - 0.2891	0.0561	0.7822	-0.2891	0.514	17.825
AC alone	y = 0.2176x - 0.1503	0.2176	0.8641	-0.1503	0.707	4.596

4. Conclusion

This study focused on the potential of FA to serve as a low cost adsorbent of MTBE and a form of waste reuse. The results showed raw-FA, modified form with Fe_2O_3 and Al_2O_3 to be ineffective in MTBE treatment with <15% removal efficiency. However, Ag_2O impregnation resulted in significant improvement in adsorption, with 24% removal efficiency. This peak adsorption was achieved using 50 mg per 100 mL of aqueous solution, and 120 min of agitation at 200 rpm. The role of Ag_2O was further studied by impregnation of AC with Ag_2O, which resulted in a drop in its MTBE adsorption from 71% to 53% removal efficiency. This observation prompted the conclusion that for a low surface area material like FA, impregnation with Ag_2O brought surface area increase, while resulting in surface area decrease in high surface area material like AC. BET analysis confirmed this with an increase from 7154 m^2/g to 16789 m^2/g and a decrease from 1126.631 m^2/g to 1039.4770 m^2/g for FA and AC respectively following Ag2O impregnation. Also, Langmuir isotherm model best represented the MTBE adsorption behaviour of both the Ag_2O impregnated FA and AC, having r-square values of 88.75% and 89.92% respectively.

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