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Investigating the removal of methyl tertiary butyl ether (MTBE) from water using raw and modified fly ash waste materials

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ABSTRACT

Classical techniques for remediation of methyl tertiary butyl ether (MTBE) from contaminated water sources are characterized by inherent limitations due to its unique physical and chemical characteristics, making further remediation researches promising. Fly ash (FA), which is a waste material derived from the combustion of coal or heavy liquid fuel has been reported to show favorable adsorption results with selected metals, dyes, and some organics in aqueous solution. In this study, raw FA, acid-treated FA, and metal oxide (silver, iron, and aluminum) impregnated FA were assessed on a bench scale, for MTBE adsorption in contaminated water system and benchmarked against activated carbon (AC). Results showed that only silver oxide (Ag_2O) impregnated FA achieved ~24% removal of MTBE from aqueous solution, while the other tested adsorbent materials achieved <10%. MTBE optimum adsorption was attained after 120 min of contact, and 0.5 g/L dosage of adsorbent. Conversely, silver oxide impregnation of AC brought about a drop in its MTBE removal efficiency from an optimum efficiency of 71 to 53%. Also, the Langmuir isotherm model best represented the MTBE adsorption behavior of both the Ag_2O-impregnated FA and AC, having R^2 of 88.75–89.92%, 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 tetraethyl 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 Koc (11 mg/L), and poor natural degradation make it persistent in the environment [1]. The

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unpleasant odor and taste of contaminated system are primary concerns associated with MTBE. Also, the US Environmental Protection Agency [2] considers MTBE to be a potential human carcinogen, with advisory level for MTBE ranging from 20 to 40 μg/L.

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 (AC) has recorded significant success in the removal of MTBE from aqueous solution, hence regarded as the established adsorbent of MTBE [3]. Studies on the use of readily available low-cost materials for the removal of environmental contaminants are considered as viable alternatives.

Fly ash (FA) constitutes the major particulate waste byproduct from burning of coal or heavy liquid fuel. It is 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 1–10 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 [4].

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 conditions 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). Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) from Fisher Scientific Company, ferric nitrate ($Fe(NO_3){\cdot}9H_2O$) from LOBA Chemic Pvt Ltd, and silver nitrate ($AgNO_3$) from Eurostar Scientific Ltd were used as sources of aluminum, iron and silver, respectively. 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 FA materials

The raw FA was treated with nitric acid in the volume ratio of 1:3 (ash: nitric acid). The mixture was stirred for 24 h at 120˚C, with an attached condenser. Segregation of phases was ensured by allowing the mixture to stand for 2 h, 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 24 h and stored until used for the batch experiments. For the modified FA, a 10% (by mass) metal oxide impregnation was carried out using aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$), ferric nitrate ($Fe(NO_3){\cdot}9H_2O$), and silver nitrate ($AgNO_3$) as sources of aluminum, iron, and silver, respectively. For each total mass of modification FA produced, mass fractions of 90% acid-treated FA and 10% metal oxide source were soaked in ethanol, followed by sonication of the mixture for 30 min, then calcination at 350˚C for 3 h, and the resultant material was stored in a dry environment 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. Following preparation, the adsorbents materials were characterized by Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM/EDS) (JOEL JSM 5900LV) and Brunner–Emmett–Teller (BET) surface area analysis (Flow Sorb II-2300, Micromeritics).

2.3. Adsorption runs

Each batch experiment was carried out in a 125-mL conical flask with a Parafilm sealing membrane, at room temperature. About 100 mL MTBE solution with 1,000 μg/L initial concentration and pH 6 was used in each run. Blank experiments were conducted to assess the loss of MTBE to the flask and environment during the sorption process. Seven 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 0.1 to 1 g/L were used for the sorption tests, with contact time from 30 to 300 min and agitation speed of 200 rpm. Duplicate 1.0 mL water samples were collected at 60 min interval in a glass vial and analyzed for MTBE concentration using GC/MS system.

2.4. Chemical analyses

The collected samples were allowed to stand for several hours at room temperature before analysis to ensure that equilibrium between the vapor phase and the liquid phase had been reached and each duplicate sample was analyzed for MTBE. A Thermo Scientific Trace GC Ultra Gas Chromatograph coupled with an ISQ single quadrupole mass spectrometer was used. Headspace technique was utilized for sample introduction, with helium as the carrier gas. A 60 m long, 0.32 mm ID, and film thickness of 1.8 μm was used for the analysis of MTBE and its byproducts. The initial GC temperature used was 50˚C (1 min) increased to 220˚C at a rate of 20˚C/min. An ISQ MS method utilized was based on EI Ion source temperature of 200˚C and acquisition time from 4.3 to 7.3 min with a detector gain of 5×10^4. Selected Ion monitoring was used for the detection and quantification of the target compound.

3. Results and discussion

3.1. Characterization of the nanocomposite materials

3.1.1. Scanning electron microscopy–energy dispersive X-ray Spectroscopy (SEM/EDS)

A SEM equipped with EDXS was used to characterize the FA and study its surface morphology. The microchemical 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 as shown in Table 1. 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.

3.2. Removal of MTBE

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 sorbate in the solution. Fig. 2 shows an 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 may be attributed to saturation of active sites on the adsorbents and a point at which desorption rate was slightly above adsorption rate [5]. The comparative study with AC also showed increase in MTBE removal with time and an optimum removal at 120 min. These 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 [6]. 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 0.5 g/L, 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 0.5 g/L may be attributed to overlapping or aggregation of adsorption sites resulting in surface area reduction [7]. Also, comparative study with AC showed increase in MTBE adsorption with dosage increase and a peak adsorption of 71% with 1.0 g/L under same experimental setup as used for the FA materials.

Table 1
Characterization of FA-based adsorbents

		Raw FA	Acid treated-FA	Ag-FA	Al-FA	Fe-FA
EDS atomic weight (%)	C	78.1 ± 1.0	80.2 ± 1.2	76.3 ± 1.0	79.2 ± 1.0	77.1 ± 1.0
	O	11.6 ± 1.1	13.4 ± 0.9	7.8 ± 0.6	7.6 ± 0.6	8.5 ± 1.0
	S	7.1 ± 0.8	6.4 ± 1.1	5.3 ± 0.4	3.9 ± 0.5	4.9 ± 0.6
	Zn	1.4 ± 1.1	–	–	–	–
	Cu	1.3 ± 1.0	–	–	–	–
	V	0.5 ± 0.5	–	–	–	–
	Ag	–	–	10.6 ± 0.7	–	–
	Al	–	–	–	9.3 ± 0.8	–
	Fe	–	–	–	–	9.5 ± 1.0
BET surface area ($m^2 g^{-1}$)		7.154	6.024	16.789	11.889	9.056

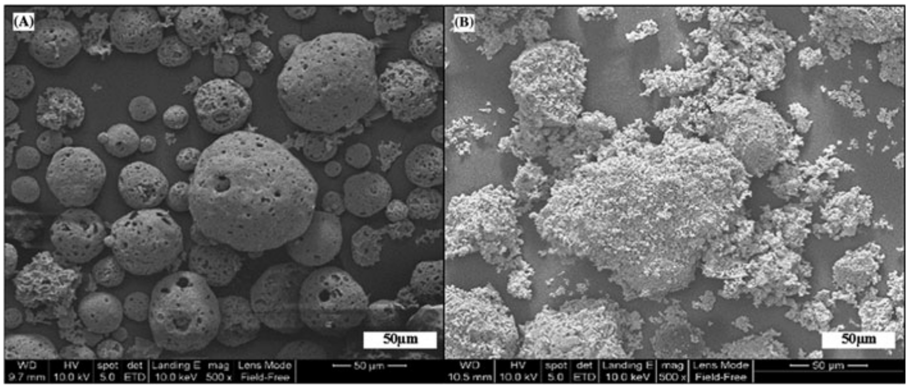

Fig. 1. SEM micrographs of raw fly ash (A) and modified fly ash, Ag_2O-FA (B).

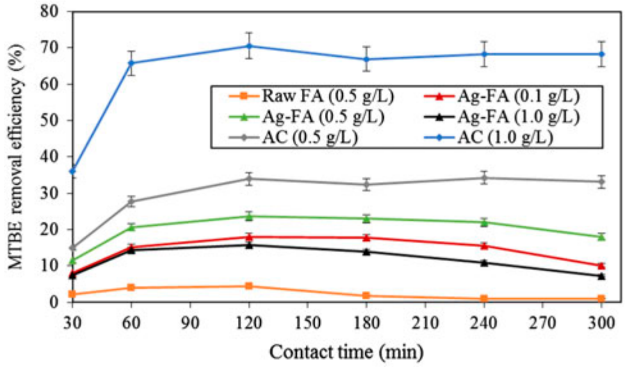

Fig. 2. Effect of contact time on MTBE adsorption behavior of the FA-based adsorbents and AC.

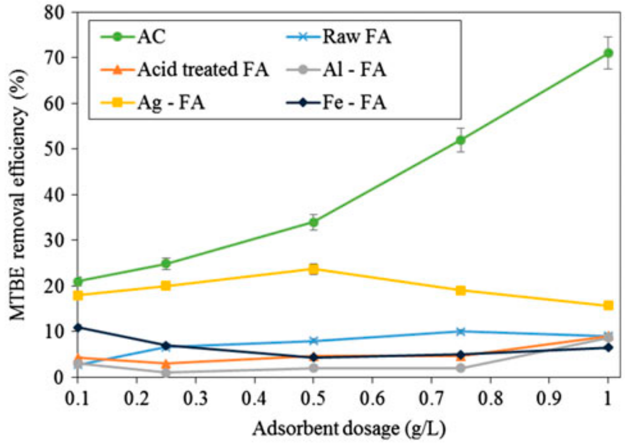

Fig. 3. Effect of adsorbent dosages on MTBE adsorption behavior of the FA-based adsorbents and AC at optimum time of 120 min.

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 [8,9]. 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% for Ag-FA, while a decrease from 71 to 53% for AC following silver oxide impregnation. The BET surface area analysis of these materials also showed an increase from 7 to 16 $m^2\,g^{-1}$ and a decrease from 1,126 to 1,039 $m^2\,g^{-1}$ for FA to Ag-FA and AC to Ag-AC, respectively. These observations prompted an assumption that the improvement in MTBE removal by Ag-FA was driven by the increase in surface area and number of active sites. Also, our GS-MS scan mode analysis of the samples following Ag-FA treatment

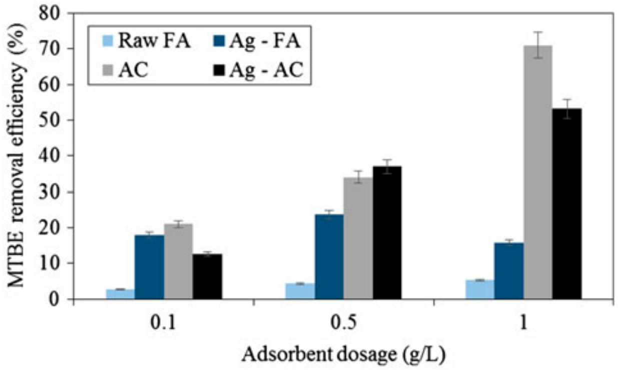

Fig. 4. Effect of silver oxide impregnation of fly ash and activated carbon on their MTBE adsorption.

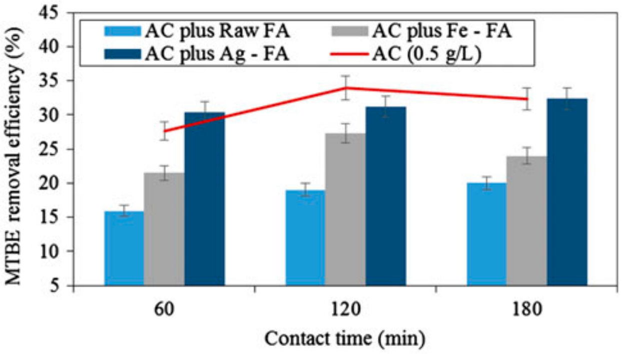

Fig. 5. Comparison of MTBE removal efficiency of AC alone with mixtures of AC and FA-based adsorbents.

showed no MTBE oxidation byproduct in the solution, prompting the deduction that the MTBE removal in this study was by physical adsorption onto active sites on the adsorbent materials.

3.2.4. Combination of AC and FA based materials

To understand the potential for synergistic removal of MTBE from aqueous solution, 0.5 g/L (1:1) mixtures of different FA-based materials and AC were tested and benchmarked with MTBE removal by 0.5 g/L of 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 the cost of impregnation, but also to the cost of FA disposal. Hence, Ag-FA could be used to reduce the amount of AC in a treatment process, thereby providing a relatively cost-effective alternative.

3.3. Adsorption isotherms study

Langmuir and Freundlich isotherms were used to assess the MTBE adsorption behavior of the silver oxide-impregnated FA in this study. Langmuir [10] 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 2 summarizes the isotherms parameters calculated from optimum adsorption of MTBE onto Ag-FA and AC.

The linearized Langmuir isotherm equation expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}} \tag{1}$$

From the above equations, C_e is the equilibrium MTBE concentration (mg/L); q_e is amount of MTBE (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); $q_{\max}$ is the theoretical maximum adsorption capacity (mg/g); and K_L is the Langmuir isotherm constant (L/mg). A linear plot of $1/q_e$ against $1/C_e$ was used to obtain the values of $q_{\max}$ and K_L from the slope and intercept.

The linearized Freundlich isotherm equation expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

From the above equations, C_e is the equilibrium MTBE concentration (mg/L); q_e is amount of MTBE (mg) adsorbed per gram of the adsorbent at equilibrium (mg/g); and K_F is the Freundlich adsorption constant related to the adsorbent adsorption capacity ((mg/g) $(L/mg)^{1/n}$). A linear plot of $\ln q_e$ against $\ln C_e$ was used to obtain the values of K_F and n from the intercept and slope, respectively [11,12].

Table 2
Isotherm parameters from optimum adsorption of MTBE onto silver oxide-impregnated fly ash and activated carbon

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

4. Conclusions

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 forms 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 0.5 g/L of adsorbent, 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 resulted in surface area increase, while resulting in surface area decrease in high surface area material like AC. BET analysis confirmed this with an increase from 7 to 16 $m^2 g^{-1}$ and a decrease from 1,126 to 1,039 $m^2 g^{-1}$ for FA and AC, respectively, following Ag_2O impregnation. Also, Langmuir isotherm model best represented the MTBE adsorption behavior of both the Ag_2O-impregnated FA and AC, having R^2 values of 88.75–89.92%, respectively.

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