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Eco-Friendly Detoxification of *Jatropha curcas* L. Biodiesel from Heavy Metals Using Date Stone Adsorbent

MONA ALNAEEM ALHASSAN[1], CHRISTINA YACOUB ISHAK[1] and M. EZELDIN OSMAN[2]*

[1]Department of Chemistry, Faculty of Science, University of Khartoum, Khartoum, Sudan.
[2]Peoples' Friendship University of Russia, Moscow 117198, Russia.
*Corresponding author E-mail: Wadalmsna3.com@gmail.com

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ABSTRACT

Tranesteification of *Jatropha curcus* L. fixed oil gave biodiesel which is having of some heavy metals, such as, Nickel, Copper, Vanadium, Arsenic and Lead with high concentration that may be released during the combustion. Thus producing significant toxic impact on the engine and environment. Pulverized date stone adsorbent efficiently detoxify the crude biodiesel. The adsorption efficiency of metals has been determined by comparing the concentration of metals in the crude biodiesel before and after the passing through an adsorbent column. The effect of variation of adsorbent dose on adsorption efficiency and percentage of adsorption has been studied. The concentration of heavy metals in the biodiesel before treatment has been found to be 5.152, 1.283, 0.291, 1.137, 2.626, and 2.428 ppm for Fe, Ni, Cu, V, As and Pb respectively. Concentrations have revealed decrease after the treatment to 0.962, 0.222, 0.0327, 0.150, 0.314, and 0.021 ppm respectively. Pulverized date stone has shown marked efficiency in removing toxic heavy metals from *Jatropha* biodiesel. Adjustment of DS weight and length of column resulted in higher percent of metal adsorption. This technique is a contribution in the betterment of fuel via an eco-friendly method.

Keywords: Biodiesel, Date Stones, Heavy Metals, Adsorption.

INTRODUCTION

Biofuels are considered in part, a solution to such issues as sustainable development, energy security and a reduction of greenhouse gas emissions. Biodiesel an environmental friendly diesel fuel similar to petro-diesel in combustion properties[1], has received considerable attention in the recent past worldwide[2]. Potentially toxic trace elements such as Lead, Copper, vanadium, Nickel and Arsenic with high level in biodiesel caused toxicity of environment[3]. Contamination of environmental compartments with organic and inorganic compounds such as metals and pesticides has motivated the development of purification and extraction methods[4]. Among several technologies, the extraction of metal ions using solid materials such as modified silica, alumina, activated carbon, and resins has been extensively investigated[5-9]. Recently bioadsorbents which produced from agrowastes may act as a significant material for heavy metals adsorption[10-14]. In this research work cheap, available, low cost, simplicity and more eco-friendly method has been applied to remove heavy metals from biodiesel by using pulverized date stone as adsorbent. The main objective of this research is determination of adsorption efficiency of pulverized date stone as adsorbent and to enhance the biodiesel synthesis from *Jatropha curcas* L. oil.

MATERIALS AND METHODS

Materials

Methanol, Hydrochloric acid, sodium hydroxide, sodium thiosulphate, glass wool, acetone and pulverized, Date stones. All chemicals used are of analytical reagent grade (AR)and used without any further purification, they were obta purchased from Sigma Chemical Co. (St.Louis, MO).

EXPERIMENTAL

Preparation of raw oil

The *Jatropha curcas* L. seeds have been collected from Blue Nile State (Aldmazien area). Fixed oil has been extracted by mechanical pressing according to the standard method described by AOAC[15].

Synthesis of biodiesel by Trans-esterification reaction using NaOH catalyst

Fixed oil 100 g, 300 g methanol and sodium hydroxide 1 g have been mixed in 1 L round bottom flask in the ratio [1: 3: 0.01] respectively. Then the mixture has been refluxed for 2 h at (65°C). After completion of the reaction, the mixture has been transferred into 1 L separating funnel, two layers were obtained, the upper was the methyl esters (ME) and the lower was the glycerol. Glycerol layer has been discarded, and the methyl ester layer was washed with hot distilled water to remove polar substance finally, the methyl ester layer was dried with anhydrous Na_2SO_4 and kept for purification and assessment[16,17].

Preparation of adsorbent

The date stones have been collected from the food manufacturing industries in a local market of Khartoum. Sample has been washed exhaustively with distilled and deionized water to remove edible part and dirt particles from the surface, and then oven dried (45°C) for 24 hours. Then date stone was ground into fine powder and kept in airtight bottle for experimental uses.

Characteristic of date stone

Date stone powder has been analyzed on (Shimadzu instrument FTIR 8400S).The Fourier transform infrared (FTIR) spectroscopy was used to determine main functional groups of the adsorbent within the range of 400-4000 cm^{-1} wave number.

Purification of biodiesel using DS adsorbent

Chromatography column of (10 cm height/1.2 cm diameter) has been packed with glass wool at the bottom, and then was packed with a bed (7.03 g) of pulverized date stone. Then (4 mL) of acetone were added to column drop wise and allowed to pass through the adsorbent bed. Next, 20 mL of biodiesel were passed to the column with a flow rate of (12 drops/min) the above steps were repeated with different weight of adsorbent and length of column to determine the effects of it on adsorption efficiency and percentage of adsorption. The experiments have been carried out at (27°C).

After terminations of the adsorption experiment, the remainingconcentrations of the metals in the biodiesel sample were determined by (ICP-AE). The percentage of adsorption (%) was calculated using thefollowing equation (1):

$$\%\ \text{Adsorption} = \frac{(\text{Ci} - \text{Cf})}{\text{Ci}} \times 100 \quad (1)$$

Where, C_i is initial concentration (mg/L) of the metal ions in the sample solution (before passing through adsorbent column), C_f is final concentrations (mg/L) of the metal ions in the sample solution (after passing through adsorbent column).

The efficiency of adsorption (mg/g) was calculated using the following equation (2):

$$q\ (\text{mg/g}) = [(\text{Ci} - \text{Cf}).V] / w \quad (2)$$

Where q is the efficiency of adsorption (mg/g), C_i is initial concentration (mg/L) of the metal ions in the sample solution (before passing through adsorbent column), C_f is final concentrations (mg/L) of the metal ions in the sample solution (after passing through adsorbent column) , V is the volume of the sample solution (L) and w is the dry weight of the adsorbent (g)[18].

Characterization of elements concentration in biodiesel before and after passing through DS adsorbent column using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AE) technique.

Instrumentation

The analytical determination of metals carried out by ICP-AE (Inductively Coupled Plasma –Atomic Emissions): ELAN 9000 (Perkin Elmer Instrument, Concord, Ontario, Canada).

Calibration

The ICP was carried out by external calibration with the blank solution and three working standard solutions (5, 10 and 20 μg/L) for all elements.

Sample preparation

Biodiesel (10 g) has been transferred into a clean gosh crucible, then has been burned using muffle furnace at 550°C for 2 hours. The ash was dissolved in10 mL concentrated hydrochloric acid, and then the extract was filtrated and transferred into 100 mL volumetric flask completed to the mark by deionized water and injected into instrument[19].

Determination of ash content of synthesized biodiesel before and after treatment

Biodiesel sample (10 g) has been placed in a clean goshcrucible and heated for 1 h at 105°C. Then carbonaceous residue has been ignited in muffle furnace at 550°C for 3 h until constant weight obtained. Then the crucible has been cooled and weighed finally the ash content was calculated.

RESULTS AND DISCUSSION

Data obtained from FTIR

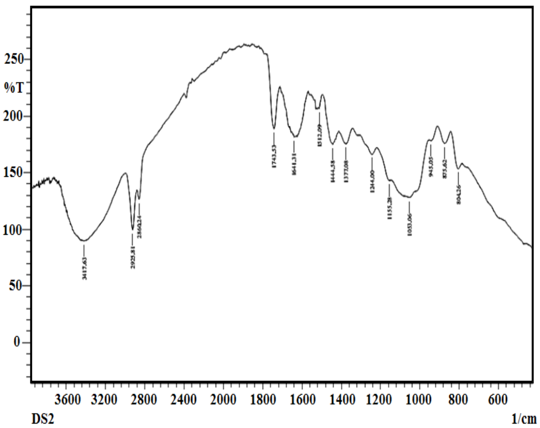

Fig.1. FTIR spectrum of pulverized DS

Figure (1) shows the FTIR spectrum of the pulverized DS. It depictssemi-broad band at the 3411.84 cm^{-1} assigned for O-H stretching mode from hydroxyl group may be involved in hydrogen bonding. Double peaks at 2866.02–2927.74 cm^{-1} due to the C-H stretching vibrations. Finally, the medium absorbance stretching peaks at 1741.60 cm^{-1} and 1643.24 cm^{-1} can be ascribed to C=O groups that are highly conjugated stretching in carboxylic groups and carboxylic moieties.

Results obtained from the ICP-AE analysis

Elements composition of biodiesel before treatment by DS adsorbent

Table 1.The elemental composition of *Jatropha curcas* biodiesel before treatment

Element	Concentration (mg/L) in biodiesel before passing through column
Na	5.157
Mg	10.156
Ca	28.782
Al	1.436
Fe	5.152
Ni	1.283
Cu	0.291
V	1.137
As	2.626
Pb	2.428

Table (1) has shown that the highest metal concentrations have been those for Ca, Mg, Na and Fe. Besides AS, Pb, Niand V metals have shown high concentration. That high concentration detected can damage fuel injection system and cause combustion chamber deposits and also might cause pollution of environment.

Elements Composition of biodiesel after treatment by DS adsorbent

The obtained results have depicted that heavy metal concentration have appreciably been decreased after treatment using pulverized DS adsorbent.

Data illustrated the effect of column length on the adsorption percentage and adsorption efficiency. It has been observed that both adsorption percentage and efficiency of adsorption has been increased when the amount of adsorbent has been doubled. In general the increase of adsorbent weight caused the increase of surface area and active sites for attraction of adsorbate.

Table 2: Elemental composition of *Jatropha curcas* biodiesel after passing through column (10 cm length/1.2 cm diameter/7.03 g of adsorbent)

Element	Concentration (mg/L) in biodiesel before pass through column	Concentration (mg/L) in biodiesel after pass through column	Percentage of adsorption %	Efficiency of adsorption (mg/g)
Na	5.157	4.309	16.44	0.00241
Mg	10.156	7.911	22.10	0.00638
Ca	28.782	24.469	14.98	0.0122
Al	1.436	1.248	13.10	0.000535
Fe	5.152	2.348	54.43	0.00797
Ni	1.283	0.857	33.20	0.00121
Cu	0.291	0.226	22.33	0.000185
V	1.137	0.806	29.11	0.000941
As	2.626	1.751	33.33	0.00248
Pb	2.428	1.625	33.0	0.00228

Table 3: Elemental composition of *Jatropha curcas* biodiesel after passing through column (20 cm length/1.2 cm diameter/14.60 g of adsorbent)

Element	Concentration (mg/L) in biodiesel before pass through column	Concentration (mg/L) in biodiesel after pass through column	Percentage of adsorption %	Efficiency of adsorption (mg/g)
Na	5.157	0.717	83.36	0.00608
Mg	10.156	0.401	96.05	0.0133
Ca	28.782	8.540	70.32	0.0277
Al	1.436	0.562	60.86	0.00119
Fe	5.152	1.203	76.64	0.00540
Ni	1.283	0.311	75.75	0.00133
Cu	0.291	0.0331	88.62	0.000353
V	1.137	0.164	86.10	0.00133
As	2.626	0.413	84.27	0.00303
Pb	2.428	0.021	99.13	0.00329

Table 4: Elemental composition of *Jatropha curcas* biodiesel after passing through column (30 cm length/1.2 cm diameter/ 21.02 g of adsorbent)

Element	Concentration (mg/L) in biodiesel before pass through column	Concentration (mg/L) in biodiesel after pass through column	Percentage of adsorption %	Efficiency of adsorption (mg/g)
Na	5.157	0.318	92.62	0.00460
Mg	10.156	0.336	96.69	0.00934
Ca	28.782	6.263	78.23	0.0214
Al	1.436	0.537	62.60	0.000855
Fe	5.152	0.962	81.32	0.00398
Ni	1.283	0.222	82.69	0.001009
Cu	0.291	0.0327	88.76	0.000245
V	1.137	0.150	86.80	0.000939
As	2.626	0.314	88.04	0.002199
Pb	2.428	0 .021	99.13	0.00229

Data from Table (3) revealed that the increase of DS weight and the length of column gave a significant improvement of both percentage and efficiency adsorption. Besides the toxic heavy metals concentrations have gone very low and lead (Pb) has almost been eradicated.

The comparison of data obtained from Table (3) and Table (4) has shown a slight increase in the percentage of adsorption of metal ions due to the increase of weight of DS, but the efficiency of adsorption has decrease, hence it can be concluded that the optimal weight and length of column were as depicted in Table (3).

Figure 3 showed the effect of adsorbent doses on the adsorption percentage. The study was carried out to optimize the required amount of the adsorbent for maximum uptake efficiency at room temperature of 27°C, and flow rate of 12 drops/minute. Percentage of Fe, Ni, Cu, V, As and Pb ions uptake by DS adsorbent increased with higher percentage from 54.43, 33.20, 22.33, 29.11, 33.33 and 33% to 81.32, 82.69, 88.76, 86.80, 88.04 and 99.13% respectively when the adsorbents doses was increased from 7.03 to 21.02 g. These results can be attributed to increase of adsorbent sites due to increase of adsorbent dose which enhancing metals removal.

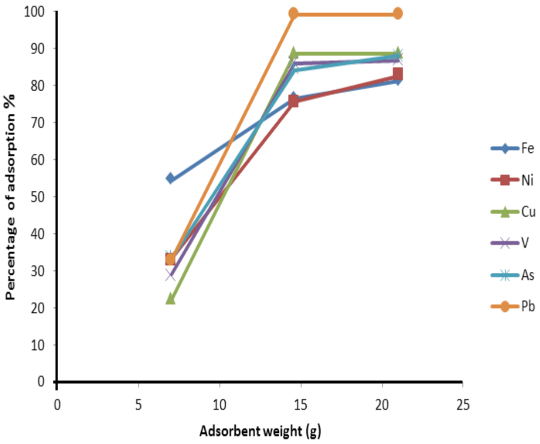

Fig. 2. Effect of adsorbent dosage on the adsorption of Fe, Ni, Cu, V, As and Pb using pulverized DS adsorbent (T: 27°C; flow rate 12 drops/minute)

Comparison between obtained results before and after passage through DS adsorbent illustrated the amount of adsorbate taken up by the adsorbent (Figure 3).

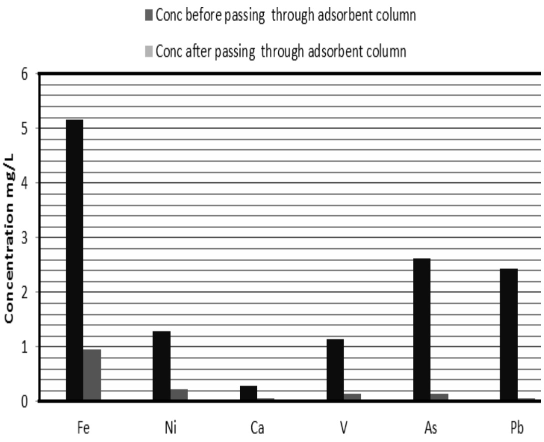

Fig. 3. Comparison between the concentration of Fe, Ni, Cu, V, As and Pb in the sample before and after passage through DS adsorbent

Adsorption is a surface phenomenon; it is a consequence of surface energy. Atoms on the surface of adsorbent are not wholly surrounded by other adsorbent atoms therefore can attract adsorbates. As depicted by FTER spectrum carboxylate anions and hydrogen bonding functionalities are site for adsorbate attraction (Fig. 1). Results also have a clarified that, the increase of surface area by the increase of mass of the rigid particles (DS) packed in a column during chromatography sorption process; the adsorbates-metal ions- are selectively transferred from the liquid phase to the surface of the pulverized date stone. The exact nature of the bonding depends on details of the species involved (Fig. 2 and 3).

Ash content of biodiesel before and after treatment with DS adsorbent

Table 5: Ash content of *Jatropha curcas* biodiesel before and after treatment

Ash content before passing through DS adsorbent (%w/w)	Ash content after passing through DS adsorbent (%w/w)	ASTM Specification for Fuel (%w/w)
0.023	0.011	Max 0.01

Data reveals the depletion of heavy metals as consequence of looking of the ash content in the biodiesel that approached the permissible limits assigned by ASTM specification[20,21].

The obtained results revealed that: the bio-adsorbent pulverized DS which has been fully characterized proved to be an efficient adsorbent. It has almost fully eradicated the toxic heavy metals The technique has led to produce biodiesel as genuine natural biofuel free off Pb element with an ash content of 0.011(% w/w).

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