International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869 (O) 2454-4698 (P), Volume-3, Issue-12, December 2015

Utilization of waste material (Part II): DMAC (De-oiled mustard cake), as an efficient adsorbent for the removal of metal cutting fluids from aqueous medium/industrial waste water

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Abstract: **An agro-based waste material de-oiled mustard cake was chemically activated with conc. H_2SO_4 to obtain a biosorbent for removal of water emulsified metal cutting fluids from aqueous medium/industrial waste water. The physic-chemical properties of Activated de-oiled mustard cake (DMAC) were characterized by bulk density, N_2 adsorption, X-ray diffraction analysis, Fourier Transform infrared spectra and scanning electro-micrograph. The adsorption tests were performed with standard oil in water emulsion of metal cutting fluid in a continuous adsorption system. The effect of varying adsorbent dose, flow rate and influent concentration were investigated and discussed. Adsorption was found to be less favorable with high influent concentration and maximum sorption capacity was obtained at low flow rate with large adsorbent dose. Isotherm study of equilibrium data of adsorption was best fitted with Langmuir isotherm model rather than Freundlich model. Total adsorption capacity q_m determined with Langmuir isotherm was 10.53g/g at 25°C. Values of R_L and R^2 also support to Langmuir isotherm model.**

Index term: **Column adsorption, Langmuir isotherm, Metal cutting fluid, De-oiled Mustard cake.**

I. INTRODUCTION

Pure and unpolluted water is a necessity of a healthy life. Now a day pollution is growing rapidly due to industrialization which bring more harmful impact than good such as water, sound and air pollution. Industrial waste effluents have threatened the water resources at present time. Toxic heavy metals, hazardous chemicals waste residual oil, dyes, waste emulsified oil etc. have developed pollution in waste water.

Emulsified metal cutting oils are used during various operations in industries such as improving surface finish, production of machined parts, reducing thermal deformation, reducing work piece, protecting tools from abrasive wear [1]. Metal cutting fluids exhibits biocides, lubricants, corrosion inhibitors, extreme pressure additives, foaming agents. This composition of metal cutting fluid contains different types of halogenated hydrocarbons. Because of these hydrocarbons the functional properties of the metal cutting oil emulsion has been lost after their usage for a certain time period [2].

About 100 million gallons of metal working fluids are used over a year in US (National Petroleum Refiners Association 1991), which must be treated before disposal due to its toxicity even at very low concentration for microorganisms, present in sewage system for biodegradation. Cutting fluid causes skin disease such as dermatitis and may be carcinogenic on regular contact. Mist generated by cutting fluid may cause respiratory disease [3]. Because of the increasing negative impact on environment and living beings, waste cutting fluids have to be treated by suitable and efficient methods before they can be allowed to flow into the municipal waste treatment plant.

Biological methods [4] may be proved insufficient to treat cutting fluid containing wastewater. Conventional treatment methods of cutting fluid (oil in water emulsion) are chemical de-emulsification [5], electro-chemical coagulation [6], reverse osmosis [7], ultrafiltration [8]. Some researchers have introduced hydrothermal oxidation [9] to treat cutting fluid but these methods consume a lot of energy and also provide insignificant results in compare to adsorption. Adsorption is an emerging technology by which oil can be removed from oil in water emulsion up to a feasible ratio. Till now used adsorbents are eucalyptus sawdust [1], white rot fungus [2], peat [10], mixed CaO-MgO [11], activated carbon [12], surfactant modified natural adsorbent like barley straw [13], chitosan [14], polymeric resin beads [15], etc.

A versatile adsorbent which has been used for removal of a broad type of pollutants such as organic, inorganic, gaseous from aqueous media is activated carbon [16]. Activated carbon is a powerful adsorbent having large surface area. But its regeneration and reuse become costly [17]. To overcome these disadvantages/complications, the researches have to move towards natural, renewable, abundant, ecofriendly and low-cost materials as alternate adsorbents. Some studies have been explored to prepare activated carbon from agro-based material such as walnut shell [18], *mangiferaindica* rinds [19], *cajanuscajan* stem [20], lemon peel [21] and pomegranate peel [22]. The results obtained from these studies are feasible and suitable for water pollution control [23], [24].

It has been studied earlier that pomegranate peel waste and pumpkin seed waste was used as an adsorbent for the removal of waste metal cutting oil from oil water emulsion waste water [22], [25]. Keeping in view the successful results of the above studies, this low cost agricultural waste product in the form of de-oiled mustard cake was attempted to convert it as an efficient adsorbent for adsorption of cutting oil. Therefore, in this study, a local agricultural, cheap, ecofriendly, abundant and solid waste material de-oiled mustard cake was selected to prepare activated carbon for the treatment of emulsified wastewater.

II. EXPERIMENTAL SECTION

A. *Adsorbate Preparation*

The adsorbate used in the present work was Metal cutting fluid (MCFs) named as IPOL Aqua Cut 125 manufactured by IPOL Lubricants, Mumbai, India and was purchased from local market. The samples of emulsified oil wastewater called adsorbate were prepared by mixing the different volume of MCFs in 100ml of deionized water with blending in an electric mixer at high speed for 10-12min, for stabilizing the solution. The resultant solution was milky white, having density 0.824g/cm^3 and viscosity 0.033Pa.s at 30ºC measured with pycnometer and ASTM D445 respectively.

B. Adsorbent Preparation

De-oiled mustard cake was collected from local oil refining mill and crushed into small pieces with the help of ball mill. Raw material was washed with distilled water continuously and then with deionized water for removal of dirt particles and water soluble bio-molecules. After thoroughly washing material were dried in sunlight until the moisture was partially evaporated. The material was further dried in hot air oven at 100ºC for 2-3h until the residual moisture was completely evaporated and showed constant weight. The activated carbon of agro-waste material were produced by using the method reported elsewhere [26]. The dried material was grounded to a fine powder and made homogeneous through 90-300µm sieve and preserved in desiccators for the activation process. They were carefully labelled as DMC.

The dried material was treated with concentrated H_2SO_4 acid in the ratio 1: 2.8 by weight and kept in an air oven at 185º±5ºC for 24 h. The carbonized material was cooled and washed several times with deionized water. After washing it was soaked in 1% $NaHCO_3$ solution for 12h for removal of residual acid and again washed with deionized water until the pH<7 was reached. Then the material was dried at 105º±5ºC for 7-8h up to constant weight and labelled as DMAC for further adsorption procedure.

C. Characterization of Adsorbent

The characteristics of DMAC adsorbent were analyzed by using conventional and analytical techniques. Moisture content was determined by using ASTM D 2867-99 Method. The total carbon yield was determined manually with the help of percentage of ratio of dried activated deoiled mustard cake (DMAC) to the weight of pre-treated DMC used in carbonization and activation process. Iodine number was determined according to ASTM D 4607-94 method and bulk density was examined by standard procedure [27]. The Brunauer-Emett-Teller (BET) equation and $p/p_o = 0.94$ were employed to obtain BET surface area and pore volume from N_2 adsorption data respectively.

D. Sorption Experiment

All experiments were conducted in a Pyrex glass column of 30mm inner diameter and 200mm long, in a downward flow of the oil in water emulsion with peristaltic pump (at fixed temperature 25ºC). Two different measured quantity of adsorbent were used in the experiment at which column have two different bed heights (40mm and 92mm). Prior to each experiment, the column filled with adsorbent was rinsed up with water to remove air bubble. The oil in water emulsion was forced through the column by a pump at three flow rates (20ml/min, 35ml/min and 50ml/min). The effect of varying operating conditions such as flow rate, column/bed height and influent concentrations (pH range 8-9) on sorption capacity of adsorbent were studied by measuring the oil concentration in effluent as a function of time.

Oil concentrations were determined by COD analysis, using reactor digestion method [28] on ELICO Double beam SL 210 UV Vis Spectrophotometer.

E. Fourier Transform Infrared (FTIR) Spectroscopy, SEM and XRD analysis

Fourier Transform Infrared Spectra of DMAC and oil loaded DMAC were collected on a Perkin Elmer Spectrum version 10.03.05 from 4000 to 400cm^{-1}.

The surface morphology of the DMAC before and after metal cutting oil adsorption were examined with a SEM (Model: Zeiss EVOMA 10) at 20kV.

X-ray diffraction study for nature of prepared activated carbons from Deoiled Mustard Cake was carried out using Philip’s Analytical Instrument (40 kW/30 mA) from 0º to 80º (2ϴ) ranges.

III. RESULT AND DISCUSSION

A. Physico-Chemical Characterization

The detailed physical characteristics of de-oiled mustard cake activated carbon (DMAC) are given in Table I. The Iodine no. and porosity of activated carbon are inter-related. Activated carbon having high iodine number (>900) also has numerically similar large surface area whereas for low surface area the correlation breaks and falls away [29]. DMAC has low surface area in compare to PGAC and PSAC both.

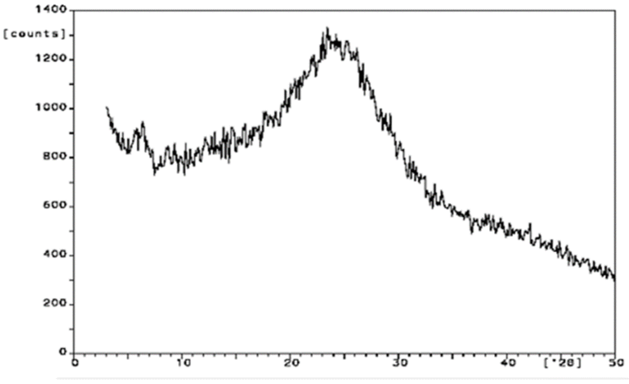
Table1. Quantitative characterization of Activated Carbon of De-oiled Mustard Cake (PSAC)

Characteristics	DMAC
Moisture Content	5.7%
Carbon Yield	3%
Iodine No.	263
Pore Volume	36.6%
Surface Area	28.2m^2/g
Bulk Density	0.869g/ml

B. XRD, FTIR and SEM

XRD pattern of DMAC before and after metal cutting oil adsorption are shown in Fig. 1(a) and (b) respectively. The appearance of a broad peak at 2ϴ~24º in Fig. 1 (a) indicated

(a)



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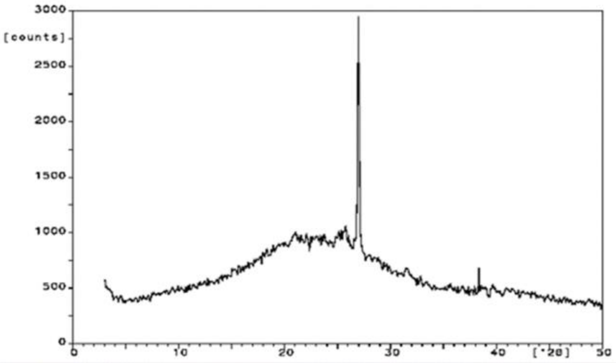
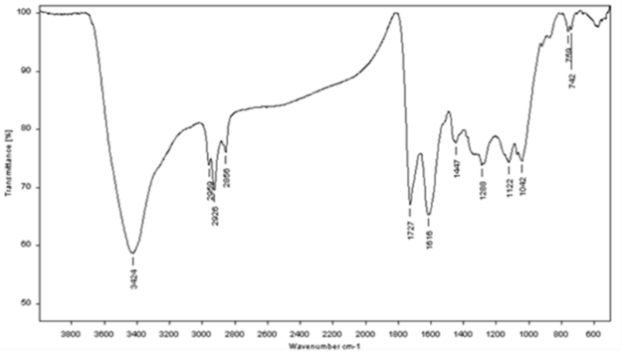


Fig. 1. X-Ray diffraction pattern of (a) DMAC before adsorption (b) metal cutting oil loaded DMAC after adsorption

that the silica present in DMAC, that was amorphous in nature [30]. It was concluded that XRD pattern for prepared de-oiled mustard cake activated carbon indicated a shape of typical amorphous carbon. The XRD analyses show that the activated carbon prepared from De-oiled mustard cake was clearly formed in amorphous state. Metal cutting oil was adsorbed on de-oiled mustard cake activated carbon after adsorption. This statement was supported by the XRD pattern of activated carbon after adsorption of cutting oil shown in Fig. 1(b). The oil loaded DMAC in Fig. 1(b) shows a little deviation in nature of adsorbent with a sharp peak at $2\Theta \sim 27^{o}$ reveals the partial crystalline nature of adsorbent DMAC.

The FTIR spectra of DMAC before and after metal cutting oil adsorption are shown in Fig.2 by spectra (a) and (b) respectively. Fig. 2(a) illustrate the functional groups and surface properties of the adsorbent by FTIR spectrum. The spectra of the adsorbent are as evidenced by the presence of a large number of peaks. The peaks obtained at 3424cm^{-1} in following Figures indicate the presence of O-H group. The peaks in the range 3000cm^{-1} – 2840cm^{-1} represent the absorption arising due to C-H stretching. Peaks at 2959cm^{-1} due to $–CH_3$ asymmetric stretching vibrations, 2926cm^{-1} due to $–CH_2$ asymmetric stretching vibrations and 2856cm^{-1} due to $–CH_2$ symmetric stretching arise. Peaks at 1458cm^{-1}, 1447cm^{-1} in Fig. 2(a) are due to $–CH_2$ symmetric bending and $–CH_3$ asymmetric bending.

(a)



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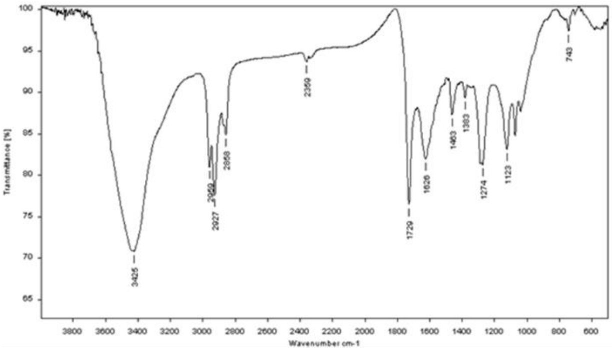

Fig 2. FTIR spectra of (a) DMAC before adsorption (b) DMAC after adsorption of metal cutting oil

The peaks in the range 1630-1600cm^{-1} of H-O-H bending mode show the presence of lattice water in adsorbent and N-H bending vibrations of primary amines is observed with the peak at 1628cm^{-1}.

The most characteristic absorption of poly-nuclear aromatics results from C-H out of plane bending vibrations of a β-substituted naphthalene of 4 adjacent hydrogen at 759cm^{-1} – 742cm^{-1} frequency. These bands can be correlated with the number of adjacent hydrogen atoms on the ring. Strong absorption due to asymmetrical C-O-C stretching in vinyl ethers occurs in the 1228cm^{-1} with a strong symmetrical band at 1041cm^{-1} or 1042cm^{-1} (1075-1020cm^{-1} range) [31]. 1072cm^{-1} – 1040cm^{-1} wave number is associated with the C-O stretching due to presence of cellulose, hemicellulose and lignin content in the activated carbon [32]. The FTIR spectra of adsorbent DMAC after metal cutting oil adsorption are shown in Fig. 2(b) spectrum contain the peaks at 1123cm^{-1} because of asymmetrical C-O-C stretching. The presence of peak at 1274cm^{-1} shows C-O-C asymmetric stretching of aryl alkyl ether group and the peak at 1382cm^{-1} shows the aldehydic C-H bending vibration. The carboxylate ion of a carboxylic acid gives rise to 2 bands: a strong asymmetric stretching band near 1650-1550cm^{-1} (at 1626cm^{-1}) and a weaker symmetrical stretching band near 1400cm^{-1}. C-N stretching band of primary amide also occurs near 1400cm^{-1}, this reveals the attachment of amido group at the surface. The presence of peak at 743cm^{-1} are due to CH_2 deformation and C-H out of plane bending. Possibility of benzoates absorb at 1729cm^{-1} due to conjugation of an aryl group or other unsaturation with the carbonyl group causes this C=O stretch to be lower than normal frequency. A weak peak visible at 2359cm^{-1} corresponds to the stretching vibration of the C-O for carbon mono-oxide or carbon dioxide derivatives.

The results shows that some peaks are shifted and new peaks are also appeared. The differences in peak position and intensity in the spectra suggested the attachment of new functional groups of metal cutting oil adsorbed at the surface of adsorbents DMAC.

The SEM micrographs of DMAC before and after adsorption of metal cutting oil are shown in Fig.3 by (a) and (b) respectively. It is clear from the micrographs that DMAC has sufficient numbers of pores on a rough and snare type structure of surface where the oil droplets may be trapped and adsorbed easily. Fig 3(b) indicates that a layer of oil has spread over the surface of DMAC.

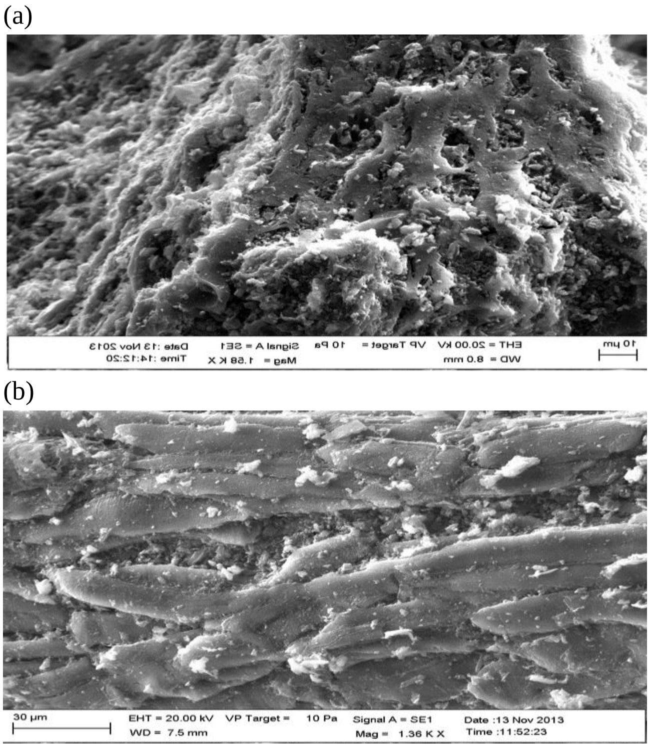

Fig.3. SEM micrographs of DMAC (a) without adsorption (b) with adsorbed metal cutting oil

The COD removal yield obtained by treating o/w emulsion of metal cutting oil with adsorption on DMAC is plotted against influent concentrations in Fig 4. For the emulsified oil, the removal yield reached a maximum value 0.835 at the influent conc. 2% and decreased progressively with an increase in influent concentration.

C. *Adsorption study in Continuous mode*

All the experimental set up with oil in water emulsion of initial concentration C_o (%v/v) = 1%, 1.5%, 2%, 2.5%, 3% were at 25ºC and introduced into the column at a certain flow rate with the help of pump. The adsorption of adsorbate through column process can be described in terms of breakthrough curves. The time to attain the breakpoint and the exhaustion point are two main characteristics for understanding the dynamic responses of an adsorption column. There is maximum sorption occurred break point reached (up to 50%) and no more possibility of adsorption remains when the curve reached at exhaustion point.

The prepared oil in water emulsion of concentration C_o=1% was introduced into the adsorption column of height 92mm with a downward flow of 35ml/min at 25ºC. The evolution of oil quantity in the effluent was tabulated and represented in Fig. 5(a), which were confirmed by breakthrough curve of adsorption system shown in Fig 5(b).

The experimental data of Fig 5 were explored that under the operating conditions (C_o= 1%, D=35ml/min, H=92mm and T=25ºC) the breakthrough volume was 8L and an equilibrium volume was at 16.45L. The holdup showed the sorption capacity would be 3.965g/g.

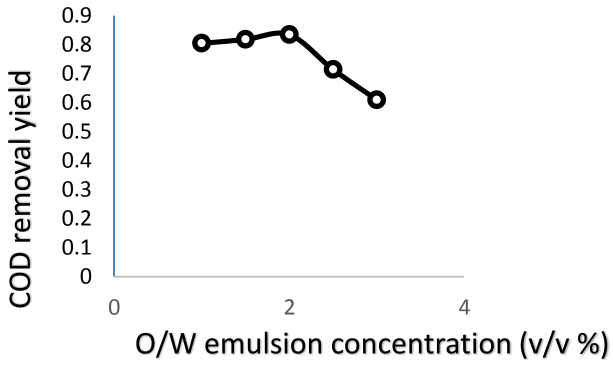

Fig 4. COD removal yield of different conc. of metal cutting O/W emulsion

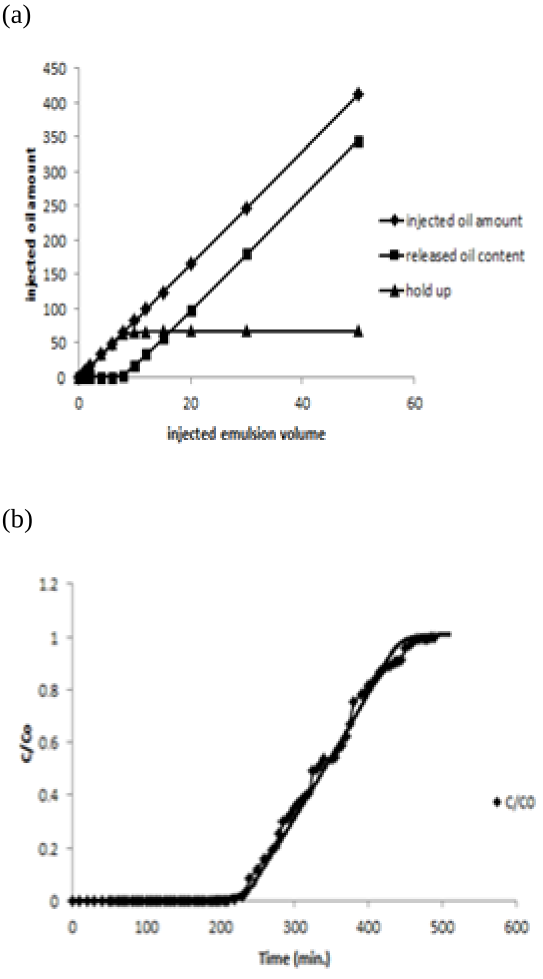

Fig 5(a) & (b). Column hold up and breakthrough curve for the adsorption of metal cutting oil on DMAC at initial conc. C_o=1.0% with bed height H=92mm and flow rate D=35ml/min.

D. *Sorption affected with emulsion flow rate (D)*

The breakthrough curves showing the effect of variation in flow rate of O/W emulsion on the column performance of adsorbents DMAC are represented in Fig. 6. The flow rate varied as 20ml/min., 35ml/min. and 50ml/min. for column of DMAC at bed height H=40mm, influent concentration C_o=1.0% at T=25ºC each. The emulsion flow plays important role in the ejection of oil quantity in the effluent at lower influent concentration C_o. As shown in figures, the breakthrough curve at low flow rate i.e. 20ml/min for DMAC have long depth adsorption zone up to breakpoint 310min. This shows the sufficient residence time of oil droplets within the column which is large enough to be entrapped and favored the maximum sorption before break point.

However, in Fig 6, at flow rate higher to a certain flow rate the adsorbent PSAC has not enough void spaces to retain more oil droplets present in the influent. As a result the break point reached earlier and a short depth adsorption zone occurred which shows the better sorption capacity of the column at low circulation flow rate.

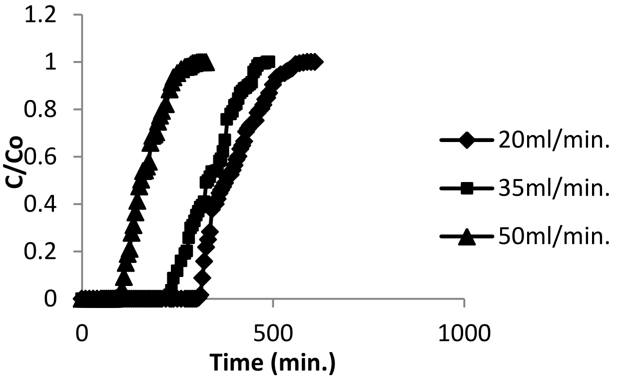

Fig. 6. Effect of varying flow rate of O/W emulsion on the adsorption of metal cutting oil on DMAC adsorbent at a fixed influent concentration C_o= 1.0%, H=40mm and T=25°C.

E. Sorption affected with column bed length

At fixed initial influent concentration at C_o=8.24g/L and 35ml/min. flow rate for the adsorbent DMAC, the bed length of 40mm and 92mm corresponding to 9g and 17g of DMAC, both were varied to study the variation effect. The breakthrough points at studied parameters of DMAC adsorbent are 105min. and 225min. respectively. As shown in Fig. 7 the large depth adsorption zone occurred in breakthrough curve of bed length 92mm. A significant change was observed in adsorption capacity with the large bed length in compare to lower one. The fact suggests large bed length provides more binding sites for adherence of oil droplets and more surface area to treat large volume of O/W emulsion because amount of adsorbent in bed was directly proportional to the surface area availability.

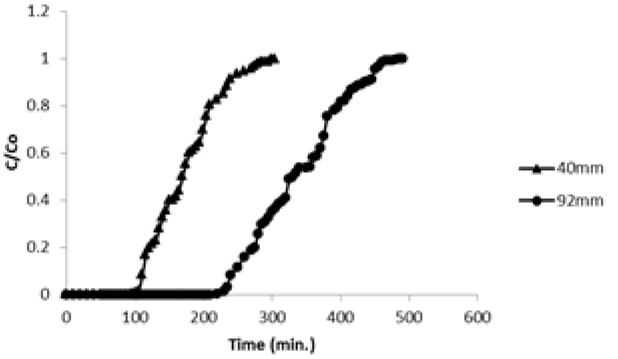

Fig. 7. Effect of varying adsorbent amount (column/ bed length H of DMAC adsorbent) of metal cutting O/W emulsion at a fixed influent concentration C_o= 1.0%, flow rate D=35ml/min. and T=25°C.

The lower bed length also has the limitations of axial dispersion phenomena, reduced solute diffusion and binding sites availability.

F. Sorption affected with variation in O/W emulsion concentration

Effect of varying initial oil concentration on the adsorption capacity of adsorbent was studied over a wide range of oil concentrations (4.12 ml/liter to 24.72 g/L). All other conditions [flow rate=35ml/min., adsorbent dose (column bed height=92mm), particle size and temperature] were kept constant and pH was maintained at the respective best value i.e. 8. It is observed that oil uptake is rapid during the initial period of adsorption and is achieved until the C/C_o=0.01 (Breakthrough point), and then very slow adsorption takes place upto C/C_o=1 (Equilibrium point). The breakthrough point for each concentration of influent (1.0%, 1.5%, 2%, 2.5% and 3%) were observed at 228min., 136min., 105min., 90min., and 70min. respectively. The equilibrium time is observed to be independent of initial oil concentration. As shown in Fig.8 the oil adsorption of DMAC at influent concentrations of 1%, 1.5%, 2%, 2.5%, 3% was 3.965, 4.96, 5.82, 6.18, 6.83g/g respectively. It is evident that the adsorption capacity didn’t show a marginal difference as the influent concentration C_o increases. At higher concentration, the number of oil molecules is relatively higher and a competitive field generates between oil droplets or available binding sites of adsorbent DMAC. Breakthrough curves shows the short depth adsorption zones at higher concentrations (as 2%-3%), which indicates the occurrence of large mass transfer in phase I of column adsorption process and earlier exhaustion.

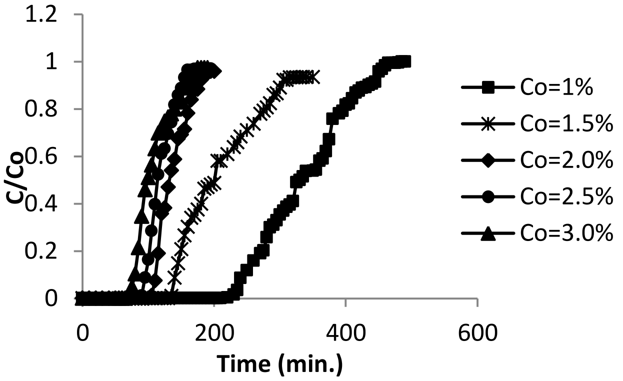

Fig. 8. Effect of varying concentration of metal cutting O/W emulsion at a fixed flow rate D=35ml/min, bed length H of DMAC adsorbent=92mm and T=25°C.

Therefore, it is concluded that the adsorption capacity decreases at higher concentration of metal cutting O/W emulsion.

G. Sorption isotherm examined

The adsorption isotherm study was conducted with the help of breakthrough curves obtained through analysis of oil removal from oil in water emulsion of metal cutting oil by plotting the curves at varying operating conditions. The influent concentration was varied from 1% to 3% at fixed bed length of 92mm, flow rate 35ml/min and T=25°C in the column process and the relative sorption capacities were measured at equilibrium and constant hold up. The adsorption of oil molecules on DMAC (solid phase) surface can be described by Langmuir and Freundlich adsorption isotherm [33].

The Langmuir isotherm model [34] assumes monolayer adsorption and usually represented as:

$$q_e = q_m b C_e/(1+bC_e) \qquad (1)$$

Linearized form of above eq. is:

$$C_e/q_e = 1/(q_m b) + C_e/q_m \qquad (2)$$

q_e = value of adsorbate adsorbed per unit weight of adsorbent at equilibrium (g/g)

q_m = maximum adsorption capacity corresponding to monomolecular layer coverage (g/g)

C_e = adsorbate concentration at equilibrium (g/L)

b = Langmuir Constant

On plotting the graph between C_e/q_e and C_e, a linear graph is obtained which has an intercept and slope corresponding to b and q_m respectively. The essential feature of the isotherm is expressed in terms of separation factor or equation parameter R_L calculated as:

$$R_L = 1/(1+b.C_o) \qquad (3)$$

C_o = initial concentration of adsorbate (metal cutting oil in water emulsion)

Value of R_L shows the favorability of isotherm [34]. $R_L=0$ indicates irreversible isotherm, $R_L>1$ shows unfavorable and $0<R_L<1$ indicates favorable isotherm.

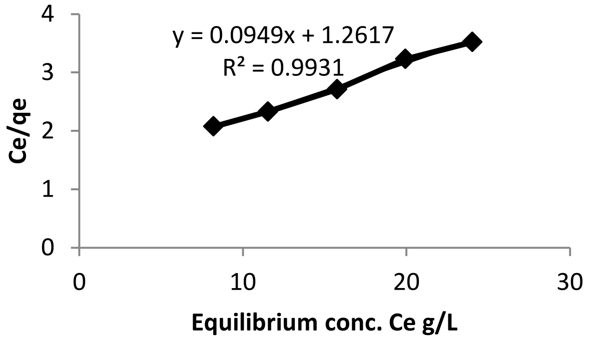

Fig 9. Linearized Langmuir isotherm curve for adsorption of metal cutting oil to DMAC

Freundlich isotherm [34] model assumes multilayer adsorption and describes the equilibrium between adsorbed metal cutting oil in water emulsion and adsorbent at a fixed temperature. Freundlich isotherm equation has the form:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

q_e = amount of removed oil per unit weight of adsorbent in g/g

C_e = adsorbate concentration in solution at equilibrium g/L

K_F = adsorption capacity

n = sorption intensity

The above eq. can be written in its linearized form:

$$Lnq_e = LnK_F + (1/n)\, LnC_e \qquad (5)$$

K_F and n values are calculated from the graph (plotted between Ln q_e and Ln C_e from the equilibrium data). The isotherm would be favorable if n>1 and also indicated the heterogeneity of adsorption process. The adsorption parameters of linearized Langmuir and Freundlich isotherm model were obtained from experimental data plotted in Fig. 9 and Fig. 10 respectively. By considering the values of regression coefficient R^2 from Table 2, both the models produced approximately same values of R^2 but it is slightly greater for Langmuir model, indicating better fitted model to the experimental data. The suitability of Langmuir isotherm model may also be supported by the fact that the active binding sites available on DMAC surface are distributed homogeneously. The total adsorption capacity q_m calculated by Fig. 9 was 10.53g/g. The essential feature of Langmuir isotherm model i.e. the separation factor R_L was also calculated with the help of Eq. 3, which gives the value of R_L in the range 0.61 lies between 0-1 also indicated the favorability of Langmuir isotherm.

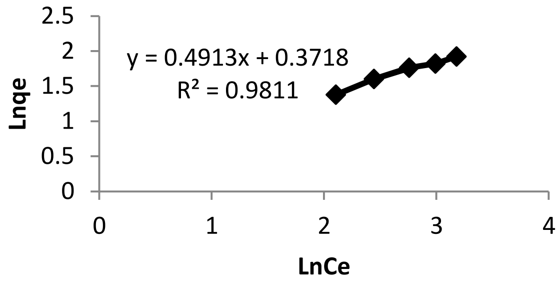

Fig 11. Linearized Freundlich isotherm curve for metal cutting oil adsorption to DMAC.

Table 2. Langmuir and Freunlich isotherm parameters with linear regression coefficient

Langmuir parameters		Freundlich parameters	
q_m	10.53g/g	K_F	1.45
B	0.0752dm^3/g	n	2.035
R^2	0.9931	R^2	0.9811

IV. CONCLUSION

The findings of the present work concludes that De-oiled Mustard cake also can be used as raw materials for the production of activated carbon by chemical activation using conc. H_2SO_4.

By analyzing the surface of prepared activated carbon after adsorption of metal cutting fluids through XRD, SEM and FTIR, the coating or film of oil was appeared on the surface of adsorbents. The experimental data showed that under studied conditions the sorption directly correlated with the mass of adsorbent H and concentration Co and reversely related with flow rate D. Langmuir adsorption isotherm shows better fitness than Freundlich isotherm. This analysis suggested monolayer adsorption of oil on homogeneous surface of DMAC. This shows the successful adsorption of metal cutting fluids on this new adsorbent, which is not more costly and easily prepared by chemical activation and also available abundantly in local area as a waste material.

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