Utilization of waste material: pumpkin seed waste, as an efficient adsorbent for the removal of metal cutting fluids from aqueous medium/industrial waste water

AntimaKatiyar, A. K. Singh, U. K. Sharma

Abstract— **Water emulsified metal cutting fluids such as mineral, synthetic, semi-synthetic are widely used as a coolant, protect work pieces and tool beds from rusting in machining operations. These fluids contain several hazardous and toxic chemicals and being discharged into wastewater streams after operations. Such wastewater having high COD value causes various diseases in human when it consumed and it is dangerous for aquatic life also. The activated carbon prepared from waste pumpkin seed is a cheap, abundantly available agricultural waste, ecofriendly and proves superior to commercial activated carbon. The activated carbon was obtained by chemical activation with conc. H_3PO_4. The adsorption of metal cutting oil has been well characterized by FTIR, SEM and Thermal analysis. Adsorption studies were conducted in column process at varying factors such as O/W emulsion concentration, flow rate and bed length. The sorption capacity of PSAC was 9.088g/g at flow rate 35ml/min with bed length 92mm for 1.5% O/W emulsion concentration. The equilibrium data of C_e and q_e are best fitted to Langmuir isotherm model with total adsorption capacity q_m of 13.85g/g. Values of R_L and R^2 also support to Langmuir isotherm model.**

Index Terms— **Column adsorption, Langmuir isotherm, Metal cutting fluid, Pumpkin seed waste, Thomas model.**

I. INTRODUCTION

All living beings exhibit their natural tendency to live a long and healthy life. For a healthy life, unpolluted and pure water is required. The rapid growth of industries is creating a lot of pollution that have the tendency to bring more harmful impact than good such as water, sound and air pollution. Industrial waste effluents have threatened the water resources at present time. Waste water has been affected by the hazardous or dangerous chemicals such as toxic heavy metals, dyes, waste residual oil, waste emulsified oil etc. which develop pollution in water.

During various industrial operations such as production of machined parts, reducing work piece, improving surface finish, reducing thermal deformation, protecting tools from abrasive wear [1] emulsifiable cutting oils are used.

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Cutting oils are generally prepared by mixing oil and organic compound with water. Cutting oil contains several chemicals such as corrosion inhibitors, biocides, de-foaming agents, extreme pressure additives, lubricants that are composed of halogenated hydrocarbons including fluoro-hydrocarbon (HFC), chlorofluorocarbons (CFCs), chlorofluorohydrocarbons (HCFCs), per fluorocarbon (PFC) etc. After using a certain period of time, cutting oil emulsion lose their functional properties and produce a toxic and hazardous fluid known as waste cutting fluid [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]. Due to the increasing concern for the negative environmental and health effects related with cutting fluid usage, 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 having large surface area was used as a powerful adsorbent. 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 pumpkin seed hull was used as an adsorbent for the removal of basic dyes and heavy metals from waste water [25, 26]. Keeping in view the successful results of the above studies, this low cost agricultural waste product in the form of pumpkin seed waste activated carbon (PSAC) 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 pumpkin seed waste was selected to prepare activated carbon for the treatment of emulsified wastewater.

II. EXPERIMENTAL SECTION

A. Adsorbent Preparation

Pumpkin is easily available in local market and its seed have been collected for two months. It was manually de-hulled after drying in sunlight. The dried hulls were washed with deionized water for removal of dirt particles and water soluble bio-molecules. It was then dried in oven at 70°C-80°C for 24h till moisture was evaporated and showed constant weight. The activated carbon of pumpkin seed waste (PSW) was produced by using the method reported elsewhere [27]. The dried PSW was treated with concentrated H_3PO_4 acid in the ratio 1: 2.8 by weight and kept in an air oven at 185°±5°C 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 105°±5°C for 7-8h and sieved to 90-300μm size and labeled as pumpkin seed activated carbon (PSAC).

B. AdsorbatePreparation

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 adsorbate samples of emulsified oil wastewater 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 30°C measured with pycnometer and ASTM D445 respectively.

C. Characterization of Adsorbent

Conventional and analytical techniques were used to determine the different characteristics of adsorbent PSAC. Moisture content was determined by employing ASTM D 2867-99 Method. The total carbon yield was determined manually by using percentage of ratio of dried APSH to the weight of pre-treated PSW 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 [28]. The Brunauer-Emett-Teller (BET) equation and p/p$_o$ = 0.95 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 25°C). 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 adsorption process 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 [29] on ELICO Double beam SL 210 UV Vis Spectrophotometer.

E. Fourier Transform Infrared (FTIR) Spectroscopy, SEM and Thermal Analysis

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

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

The Thermal degradation behavior of the prepared activated material (PSAC) and the material after adsorption was studied using a Perkin Elmer thermal analyzer (TGA). Experiments were conducted in the temperature range of 30°C- 995°C under a N$_2$ gas flow at 20ml/min and at scanning rate 10°C/min.

III. RESULT AND DISCUSSION

A. Physico-Chemical Characterization

The detailed physical characteristics of pumpkin seed activated carbon (PSAC) are given in Table 1. 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 [30]. PSAC has low surface area in compare to PGAC.

Table1. Quantitative characterization of Activated Carbon of Pumpkin Seed (PSAC)

Characteristics	PSAC
Moisture Content	5.20%
Carbon Yield	34%
Iodine No.	348
Pore Volume	0.352 cm^3/g
Surface Area	567.75 m^2/g
Bulk Density	0.782g/ml

B. FTIR, SEM and Thermal analysis
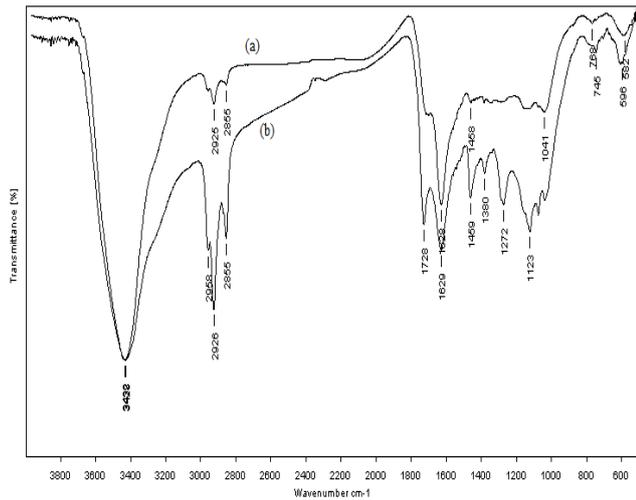
Fig 1. FTIR spectra of (a) PSAC before adsorption (b) PSAC after adsorption of metal cutting oil

The FTIR spectra of PSAC before and after metal cutting oil adsorption are shown in Fig.1 by spectra (a) and (b)respectively. Both the spectra contain peaks at $3428cm^{-1}$ (-OH stretch), $2925cm^{-1}$ (C-H stretch), $2958\text{-}2855cm^{-1}$ (adsorption peak of aromatic, aliphatic and olefinic –C-H vibrations), $1628cm^{-1}$ ($-NH_2$ deformation), $1458cm^{-1}$ ($-CH_2$ deformation), $1041cm^{-1}$ (C-O stretch). The spectrum (b) contains some distinct peaks at $1726cm^{-1}$ (characteristic absorption peak of aldehydic group), $1380cm^{-1}$ (bending vibration of aliphatic C-H), $1272\text{-}1123cm^{-1}$ (aromatic =C-H in plane deformation), $745cm^{-1}$ (C-H bending). The results show 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 to the surface of PSAC through adsorption.

The SEM micrographs of PSAC before adsorption and after metal cutting oil adsorption are shown in Fig.2 by (a) and (b) respectively. It is clear from the micrographs that PSAC 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 2(b) indicates that a layer of oil has spread over the surface of PSAC.

(a)

(b)
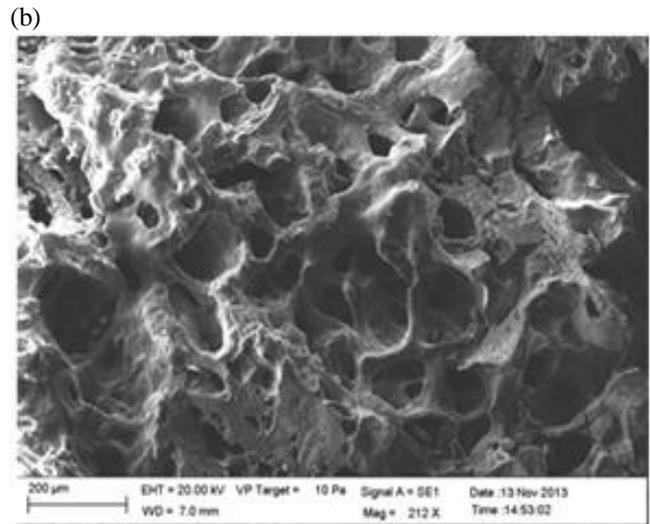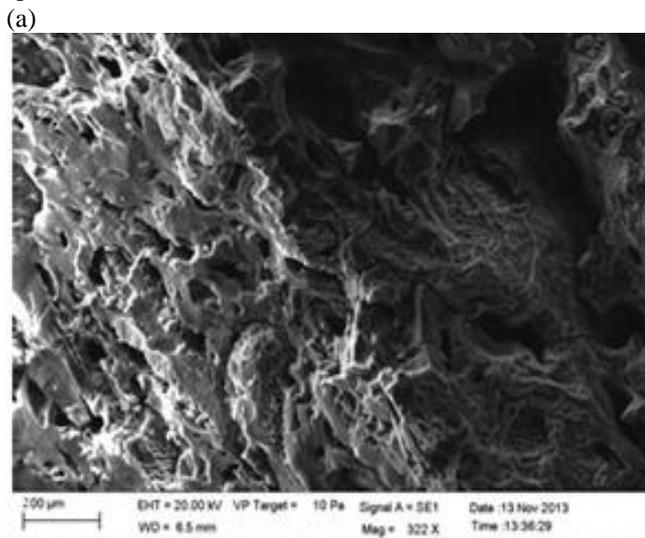
Fig.2. SEM micrographs of PSAC (a) without adsorption (b) with adsorbed metal cutting oil

Thermal analysis of prepared adsorbent (PSAC) before and after adsorption are shown in Fig 3 (a) & (b). It is depicted from the Fig 3(a) that the first weight loss of PSAC was found to be 12.57% at 88ºC because of the loss of surface water molecule which was more than the % amount found in Fig 3(b). This is due to the attachment of moisture from the atmosphere. The next loss in weight in Fig 3(a) was occurred at 400ºC-1000ºC due to gaseous vaporization asappeared in Fig 3(b). A different line of weight loss of 29.348% at the onset temperature 200-300ºC was shown in Fig 3(b) which indicates the decomposition of oil, adsorbed on PSAC surface. These differences imply that the successful adsorption of MCFs on PSAC surface.

(a)

(b)
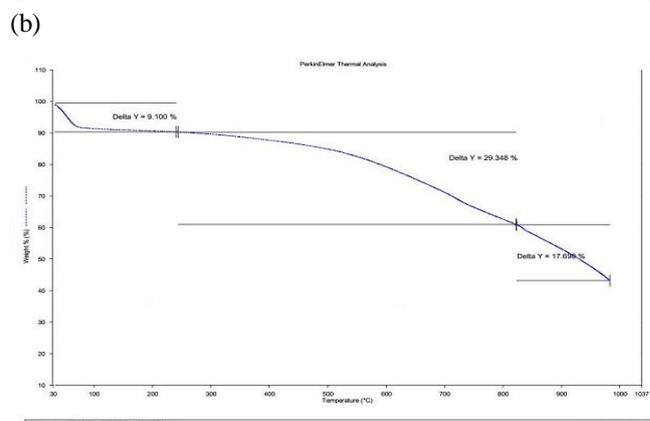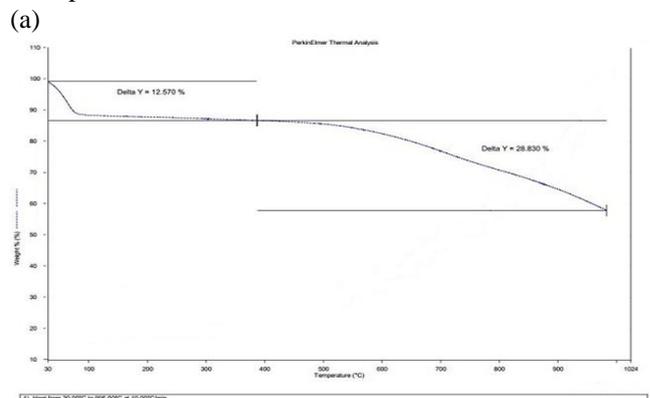
Fig 3. Thermal analysis (TGA) curves (a) before adsorption and (b) oil loaded PSAC

The COD removal yield obtained by treating o/w emulsion of metal cutting oil with adsorption on PSAC is plotted against influent concentrations in Fig 4. For the emulsified oil, the removal yield reached a maximum value 0.85 at the influent conc. 2% and decreased progressively with an increase in influent concentration.
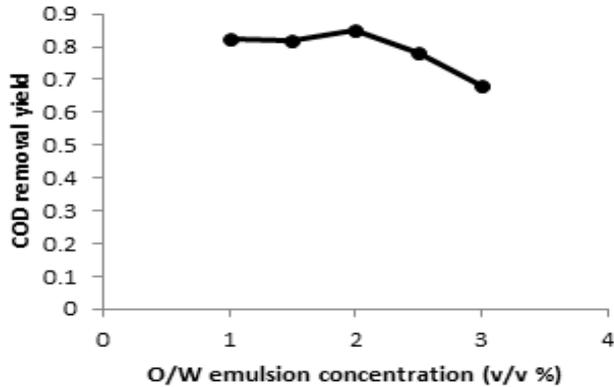
Fig 4.COD removal yield of different conc. of metal cutting O/W emulsion

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 25°C 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 till 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=1.5% was introduced into the adsorption column of height 92mm with a downward flow of 35ml/min at 25°C. The evolution of oil quantity in the effluent was tabulated and represented in Fig. 5, which were confirmed by breakthrough curve of adsorption system shown in Fig 6.
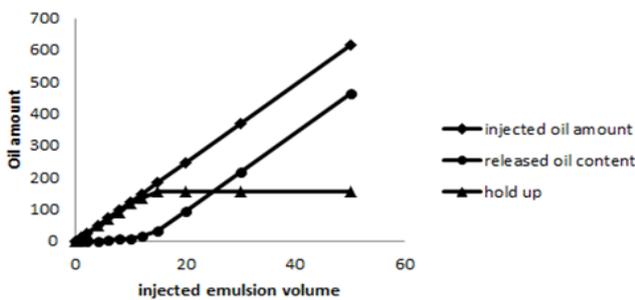
Fig 5. Column hold up evolution during adsorption of Influent conc. C_o=1.5% at 35ml/min.

The experimental data of Fig 5 were explored that under the operating conditions (C_o= 1.5%, D=35ml/min, H=92mm and T=25°C) the breakthrough volume was 5.11L and an equilibrium volume was at 15.4L. The holdup showed the sorption capacity would be 9.088g/g.

D. Sorption affected with emulsion flow rate (D)

The influence of flow rate on the column performance was examined at fixed influent concentration C_o = 1.5% and column height H = 40mm by varying flow rates as 20ml/min, 35ml/min and 50ml/min. At low flow rate, oil amount in the emulsion was low and the residence time of oil droplets within the column was large enough to beentrapped which favored the maximum sorption before break point.
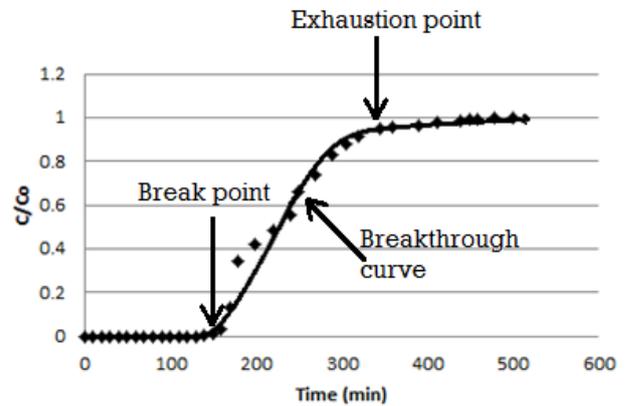
Fig 6. Breakthrough curve of adsorption process of influent conc. C_o=1.5% at 35ml/min.

However, in Fig 7, 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.
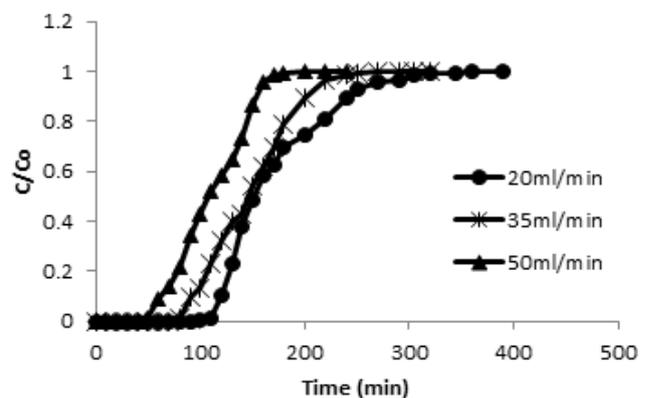
Fig 7. Effect of flow rate at fixed C_o = 1.5%, H = 40mm and T =25°C.

E. Sorption affected with column bed length

The effect of bed length for influent concentration C_o = 1.5% was studied at flow rate 35ml/min. As shown in Fig 8 the large depth adsorption zone occurred in breakthrough curve of bed length 92mm. A significant change of 2.311g/g 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 of bed. 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

Fig 9 depicts the influence of different concentration of metal cutting O/W emulsion on adsorption capacity of PSAC adsorbent at bed length 40mm with fixed flow rate 35ml/min and T= 25°C.
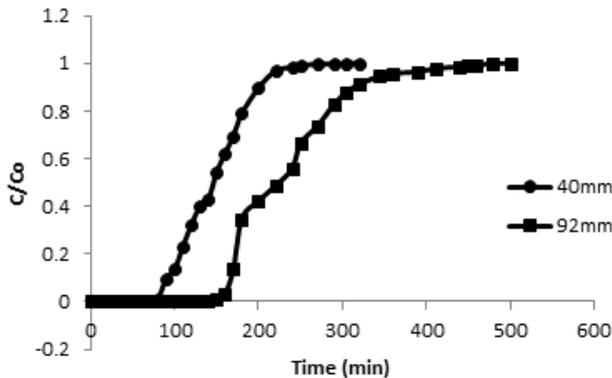
Fig 8. Effect of different bed length at fixed influent conc. Co=1.5%, flow rate D=35ml/min and T=25°C.

The oil adsorption of PSAC at influent concentrations of 1%, 1.5%, 2%, 2.5%, 3% was 5.876, 6.777, 8.33, 8.968 and 9.325g/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 PSAC. 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. Therefore, it is concluded that the adsorption capacity decreases at higher concentration of metal cutting O/W emulsion.
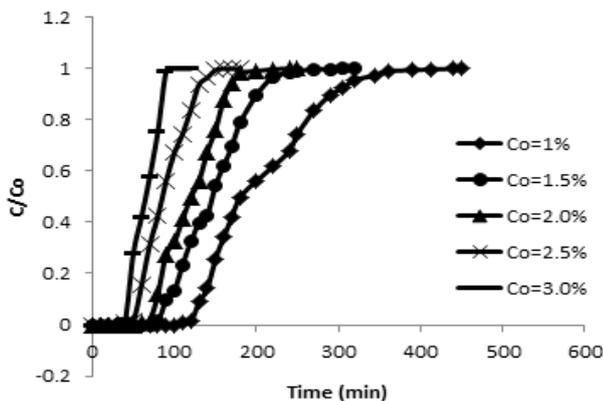
Fig 9. Effect of different metal cutting O/W emulsion concentration at fixed flow rate D=35ml/min, bed length H=40mm and T=25°C.

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 40mm, 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 PSAC (solid phase) surface can be described by Langmuir and Freundlich adsorption isotherm [31].

The Langmuir isotherm model [31] assumes monolayer adsorption and usually represented as:

$q_e = q_m b C_e / (1 + b C_e)$ (1)

Linearized form of above eq. is:

$C_e / q_e = 1/(q_m b) + C_e / q_m$ (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:

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

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

Value of R_L shows the favorability of isotherm [32]. $R_L=0$ indicates irreversible isotherm, $R_L>1$ shows unfavorable and $0<R_L<1$ indicates favorable isotherm.
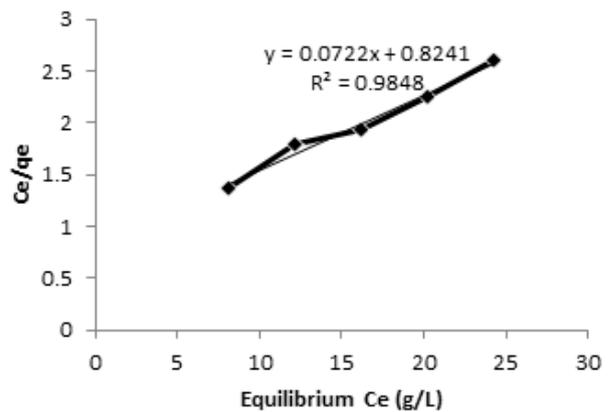
Fig 10. Linearized Langmuir isotherm curve for adsorption of metal cutting oil to PSAC

Freundlich isotherm [31] 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:

$q_e = K_F C_e^{1/n}$ (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:

$Ln q_e = Ln K_F + (1/n) Ln C_e$ (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

10 and Fig 11 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

H (mm)	D (ml/min)	C_o(%v/v)	Q_o(g/g)	K_{Th}	R^2
40	20	1.5	4.92	0.00284	0.9097
40	35	1.5	7.066	0.00369	0.9769
40	50	1.5	7.43	0.00495	0.9401
92	35	1.5	6.44	0.00218	0.8963
40	35	1.0	6.78	0.00362	0.9421
40	35	2.0	7.836	0.00378	0.9651
40	35	2.5	7.388	0.00386	0.9481
40	35	3.0	6.204	0.00587	0.9399

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 PSAC surface are distributed homogeneously. The total adsorption capacity q_m calculated by Fig 10 was 13.85g/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 0.58078-0.31591 at varying influent concentration C_o 1%-3%. The R_L value lies between 0-1 also indicated the favorability of Langmuir isotherm. Thomas Model was also examined to the experimental data due to the fitness of Langmuir adsorption isotherm.

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

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

Langmuir parameters		Freundlich parameters	
q_m	13.85g/g	K_F	2.29
B	0.0876	1/n	0.4477
R^2	0.9848	R^2	0.9739
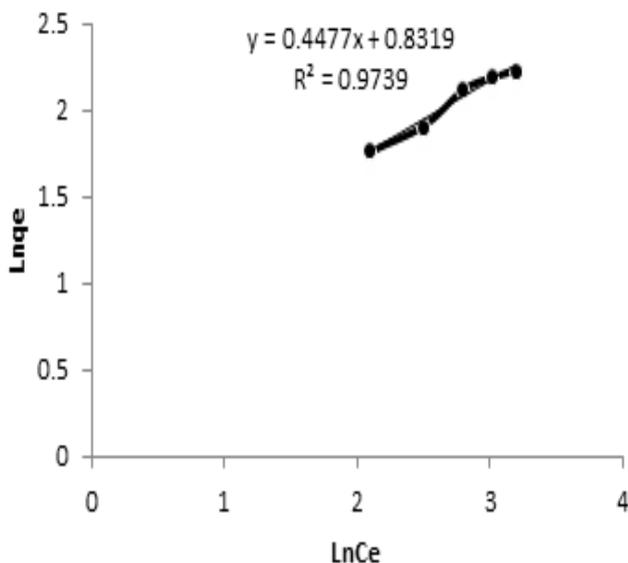
H. Thomas Model isotherm

Thomas model may also apply to know about adsorption capacity, predict breakthrough curve and the column performance in a fixed bed column. This model assumes Langmuir isotherm and second order reversible kinetics [31]. The linear form of Thomas model is represented as:

Ln [(C_o/C)-1]=[($K_{Th}Q_om$)/D] – ($K_{Th}C_ot$) (6)

Q_o = max. adsorbate concentration per unit mass of adsorbent
M = amount of adsorbent
K_{Th} = Thomas rate constant
D = flow rate

By plotting Ln[(C_o/C)-1] against t the values of K_{Th} and Q_o were calculated and tabulated in Table 3 (plots are not given).

Table 3. Calculation of Thomas parameters at varying operating conditions of column adsorption system

Table 3 shows the total adsorption capacity of PSAC at varying operating conditions. As we have been observed in earlier investigations [1, 22] that the adsorption capacity Q_o

y = 0.4477x + 0.8319
R^2 = 0.9739

reduced at high flow rate, increased with increasing bed height. On the other hand by applying Thomas isotherm model, the adsorption capacity Q_o decreased from 7.43 to 6.44g/g and increased from 4.92 to 7.43g/g with increasing bed height and flow rate respectively. This reverse trend indicates that Thomas model assumes Langmuir isotherm only but does not possess the second order kinetics for this system. Therefore, Thomas isotherm model cannot be fitted for this system.

IV. CONCLUSION

Activated carbon prepared from pumpkin seed waste has been explored as a good adsorbent to effectively remove metal cutting fluid from aqueous medium/ industrial waste water at ambient temperature and neutral pH conditions. The experimental data showed that under studied conditions the sorption directly dependent on the mass of adsorbent and reduced at higher flow rate and concentration. Higher COD removal yield has been obtained at 2% v/v of influent concentration. Adsorption isotherm analysis suggested the monolayer adsorption of oil on homogeneous surface of PSAC due to the better fitness of Langmuir isotherm than the Freundlich isotherm. Therefore, present study shows an economic and prominent alternative towards the wastewater treatment technology.

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