

# A new efficient method for removal of metal cutting fluids from machining waste water

Antima Katiyar, A. K. Singh, L. K. Singh

**Abstract**— Metal cutting fluids are liquid used in machines in the form of emulsified oil for cutting, cooling and lubrication operations. Spent metal cutting fluids in the emulsified form are liberated in the environment through machining waste water which become contaminated by microorganism and produce drastic problem of water pollution. To reduce its polluting and health hazard potential, adsorption tests were performed with metal cutting fluids. Cheaper agro-residues are gaining importance for removal of various hazardous chemicals. Pomegranate peel activated carbon was successfully utilized in removing waste metal cutting oil from machining water way stream. Pomegranate peel activated carbon was prepared by chemical activation with concentrated  $H_2SO_4$ . The FTIR, SEM and XRD techniques were used for qualitative analysis of adsorption of waste metal cutting oil on pomegranate peel activated carbon. Column adsorption studies were performed by varying adsorbate concentration, influent flow rate and adsorbent bed height. It was found that adsorbate concentration (0.5%), pH 8-9 and flow rate (25ml/min) of waste metal cutting oil favored its removal from machining waste water in significant amount using bed height (60mm) of pomegranate peel activated carbon. It was observed that the experimental and equilibrium data as obtained followed the Freundlich isotherm. The  $K_F$  and  $n$  values were obtained as 3.555 and 1.77 respectively.

**Index Terms**— Adsorption, Freundlich isotherm, Metal cutting oil, Pomegranate peel.

## I. INTRODUCTION

Water pollution is one of the gravest environmental issues because it can cause problem to clean water production and also can contribute to the shortage of clean water supplies. Water pollution by oil has left an undesirable impact on the environment. Emulsifiable or water-miscible metal cutting fluids are used in metal working industries as lubricants and coolants yielding better surface finishes and tools protection from abrasive wear. Major industrial sources of metal cutting fluids (MCFs) waste, including metal manufacturing, machining and food processors. MCFs consist of a suspension of oil droplets in water, stabilized by surfactants, and usually contain several compounds such as biocides, defoamers, rust inhibitors, anti-wear agent etc. [1] Once MCFs have been used for a period, its degradation with time is unavoidable and it generates toxic liquid known as waste metal cutting fluid. Industrial waste water must be

treated before its disposal because of the toxic and hazardous properties of their component. The presence of oil in water not only induces harmful effects to aquatic life but also causes severe problems to wastewater treatment plants [2, 3] Till date, there are many treatment technologies relating to the removal of MCFs from industrial and machining waste water classified as physical, chemical and biological treatment [4]

It is therefore necessary to investigate, develop and improve known techniques. The best available technologies for oil removal include biological and physico-chemical treatment, adsorption is considered to be most potential due to its high efficiency and ability to separate wide range of organic/inorganic chemicals from water way stream [5, 6] Studies were also available on the use of adsorbents for removal of MCFs from effluents. Commercial activated carbon is widely used for adsorbing waste MCFs (emulsified oil) from industrial waste water. Many researchers have been focused on the use of solid waste, cheap and abundant natural product such as  $MgO - CaO$ , sawdust [7], walnut shell [8] and mango rinds [9] as adsorbents. MWFs contain organic matter about 50000-80000 mg/l COD [7], therefore, Viraraghavan has been reported an efficient process for removal of emulsified oil by deep bed filtration [10] Pomegranate peel is an easily available byproduct from juice making industry and it exhibits good adsorbent characteristics for the treatment of waste water containing heavy metals and dyes [11]

The continuous adsorption process is more applicable in real water treatment industries due to its low operating cost and ability of columns to adapt versatile process [12] With high volume of waste water to be treated, continuous process is a lot more time efficient than batch treatment process. Most of the reported studies on the adsorption of emulsified oil by activated carbon were conducted in batch studies [13] The limited literature on adsorption of oil in water emulsion as pollutant from effluent is the motivation to embark on this research to investigate other means of alleviating it. This study is aimed at the performance of activated carbon prepared from pomegranate peel as an adsorbent for the treatment of oil in water emulsion of waste metal cutting oil used in metal working operations and also the effect of different operating conditions using column process.

## II. MATERIAL AND METHOD

### A. Adsorbate

Commercial metal cutting fluid used in this study is IPOL Aqua Cut 125 manufactured by IPOL lubricants, Mumbai, India. This is an emulsifiable coolant which prevents rusting of work piece, machine tool beds and provides even surface for working. Oil in water emulsions

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were prepared by mixing the different volume % of oil with deionized water and blended at a high speed for 15-20 min for stabilization. Finally the oil in water emulsions were appeared milky white and having pH 8-9. The density of oil at 30°C was 0.824g/cm<sup>3</sup> determined by weighing a known volume of oil in a pycnometer. Viscosity of oil was 0.033pa.s measured according to ASTM D445.

*B. Adsorbent*

The Pomegranate peel was cut into small pieces, washed with distilled water continuously with deionized water and dried in sunlight until the moisture was partially evaporated and was further dried in hot air oven at 70°C for 24h until the residual moisture was completely evaporated. The dried material was kept safely as raw material for the preparation of activated carbon. One part of dried pomegranate peel was treated with thrice (by weight) of concentrated H<sub>2</sub>SO<sub>4</sub> acid and kept carefully in an hot air oven at 200°C±5°C for 24h under deep observation. After carbonizing the material, it was washed about 6 times with distilled water and then washed with 1% NaHCO<sub>3</sub> solution, thereafter, soaked in 1%NaHCO<sub>3</sub> solution overnight for neutralization. The material then washed with deionized water until the pH becomes <7 and dried it at 100°C±5°C in oven [14] The dried material labelled as pomegranate peel activated carbon (PGAC) was grounded, homogenized and sieved to 90-300 µm particle size and preserved in desiccator for further process.

*C. Continuous Adsorption Studies*

All column experiments were conducted in a Pyrex glass column of 3cm inner diameter and 20cm long, in a downward flow of the oil in water emulsion with peristaltic pump (at 25°C fixed temperature)for monitoring the flow rates. A measured quantity of adsorbent was placed in column at different filter bed heights (36mm and 80mm). Prior to each experiment, distilled water was passed through the column to remove impurities and air bubbles. Oil concentration in effluent was measured as a function of time with varying operating conditions such as different flow rates (25ml/min, 50ml/min), varying influent concentrations (pH 8-9) and amount of adsorbent for thorough study of adsorption process.

The mechanism of non- ideal adsorption on heterogeneous surface is generally described by Freundlich adsorption isotherm. Due to presence of different functional groups on the surface of adsorbent and various adsorbate-adsorbent interactions, heterogeneity of surface occurred. Freundlich isotherm model describes the equilibrium between adsorbed metal cutting oil in water emulsion at a constant temperature. Freundlich isotherm equation has the following form:

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

where,

- q<sub>e</sub> = oil removed per unit weight of adsorbent in g/g
- C<sub>e</sub> = oil concentration in solution at equilibrium g/L
- K<sub>F</sub> = adsorption capacity
- n = sorption intensity

Linearized form of (1) is as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

The plot between Ln q<sub>e</sub> and Ln C<sub>e</sub> from the equilibrium data gives a straight line with generating K<sub>F</sub> and n values from intercept and slope respectively.

Oil concentrations were determined by COD analyses, carried out by reactor digestion method [15] using Elico Double beam SL 210 UV Vis Spectrophotometer. Infrared spectra of dried pomegranate peel activated carbon (PGAC) and oil loaded PGAC were recorded by using a Perkin Elmer Spectrum version 10.03.05 from 4000 to 400cm<sup>-1</sup>. X-ray diffraction study for nature of PGAC was carried out using Philip’s Analytical Instrument (40 kW/30 mA) from 0° to 80° (2θ) ranges and for the surface texture details of the PGAC was observed with SEM (Model: Zeiss EVOMA 10) at 20kV before and after adsorption of metal cutting oil.

III. RESULT AND DISCUSSION

**Table. 1. Comparison of physical characteristics of various sorbent materials**

Characteristic	Pomegranate peel AC	Walnut shell AC	MgO.CaO activated with HCl
Iodine no.	745	-	-
Molasses no.	590	-	-
Surface area	820m <sup>2</sup> /g	0.171m <sup>2</sup> /g	11.70m <sup>2</sup> /g
Total pore volume/porosity	87.80%	52%	26.60%
Density	0.346g/cm <sup>3</sup>	0.64 kg/l	-
Moisture	2%	1.97%	-

*A. Characterization of adsorbent*

The average physical characterization of adsorbent is given and compared with MgO.CaO activated with conc. HCl and Walnut Shell activated carbon in Table 1. The surface area and total pore volume were determined using Brunauer–Emett–Teller (BET) isotherm by N<sub>2</sub> adsorption isotherm [15]

*B. FTIR, XRD and SEM of PGAC*

FTIR spectrum of activated carbon before metal cutting oil adsorption is shown in Fig.1, having distinct peaks at 3921cm<sup>-1</sup>-3418cm<sup>-1</sup> might be due to NH, OH or CO groups.

The FTIR spectra of metal cutting oil loaded PGAC shows (Fig.2) peaks at 3426cm<sup>-1</sup> (OH stretch), 2959cm<sup>-1</sup>, 2927cm<sup>-1</sup>, 1460cm<sup>-1</sup> and 1382cm<sup>-1</sup> indicate the presence of CH, CH<sub>2</sub> and CH<sub>3</sub> groups in the fiber. 1729cm<sup>-1</sup>-1620cm<sup>-1</sup> (CO stretch), 1072cm<sup>-1</sup>-1040cm<sup>-1</sup> wave number is associated with the C-O stretching due to presence of cellulose, hemicellulose and lignin [17]

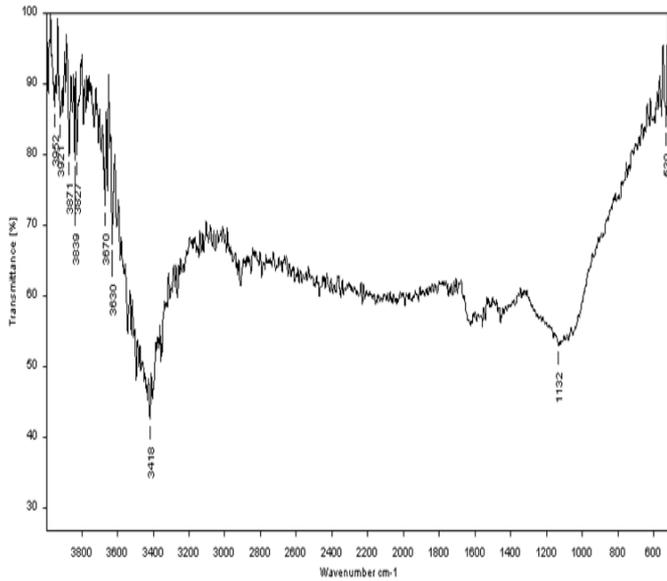


Fig. 1. FTIR Spectrum of Pomegranate Peel Activated Carbon

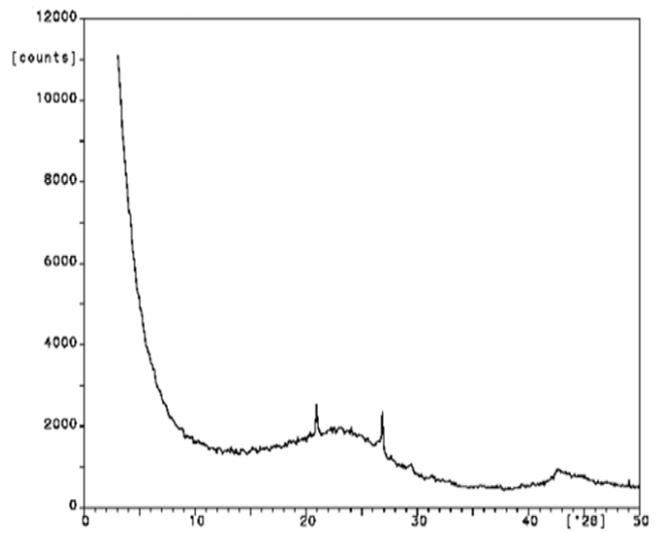


Fig. 3. XRD Pattern of PGAC before Adsorption

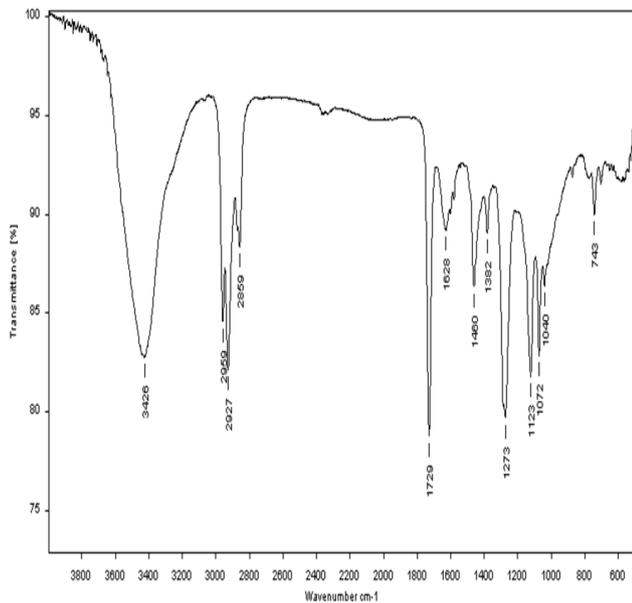


Fig. 2. FTIR Spectrum of Metal Cutting Oil loaded PGAC

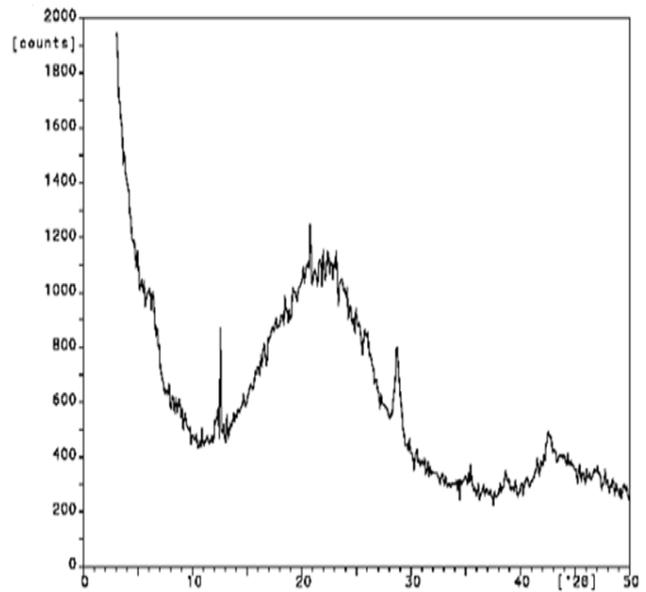


Fig. 4. XRD Pattern of Metal cutting oil loaded PGAC

The resulting FTIR spectrum after adsorption indicates that some new peaks are also detected which shows the possible involvement of different functional groups due to the successful adsorption of metal cutting oil on the surface of PGAC.

The XRD images of PGAC before and after adsorption are shown in Fig.3 and Fig.4 respectively. The amorphous nature of PGAC was determined with intensity of the observed rays with respect to scattering angle  $2\theta$ . The difference between Fig.3 & Fig.4

indicates the slight change in the intensity after loading MWFs cutting oil on the surface of PGAC. The surface morphology of the PGAC was observed with SEM before and after adsorption of metal cutting oil. It is clear from the Fig.5 that activated carbon has considerable number of heterogeneous pores on the surface, which are covered with a layer of metal cutting oil shows in Fig.6. It signifies that PGAC has good capability to trap and adsorb the metal cutting oil.

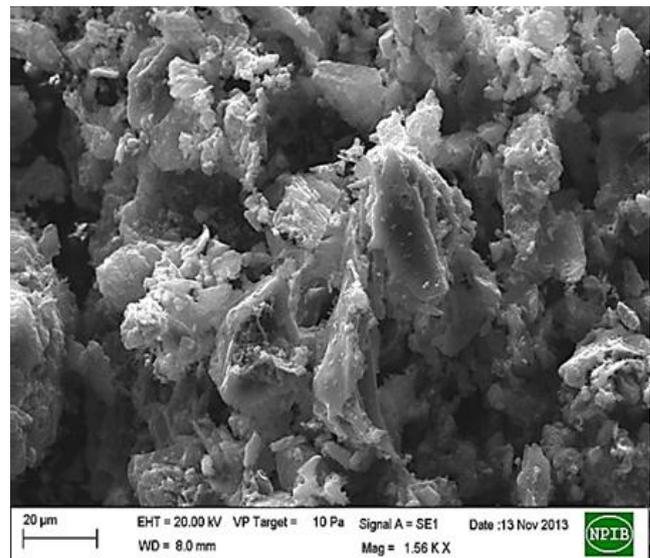


Fig.5. SEM image of PGAC before metal cutting oil adsorption

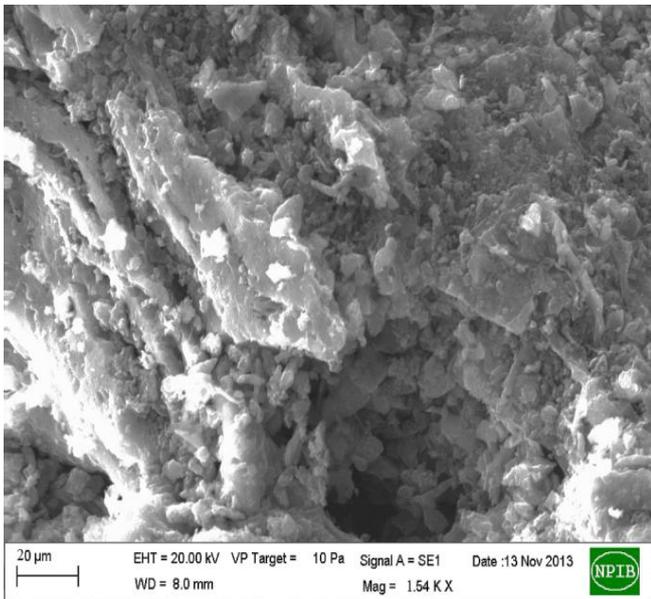


Fig.6. SEM image of PGAC after metal cutting oil adsorption

A. Continuous adsorption study

The experiments were set up with oil- in- water emulsions at different initial concentrations ( $C_0$ ) 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% at 25°C and introduced in the column with a piston flow. The chemical oxygen demand (COD) in the effluent follows the same pattern as oil concentration. The oil quantity in the effluent was evaluated by COD analyses. There was high COD reduction (98%) obtained when approximately 100% oil removal occurred in the effluent. The dynamic behavior of a filter bed column is described in terms of the breakthrough curve. The appearance of breakthrough curve and the time to attain the breakthrough point are two main characteristics for determining the operation and the

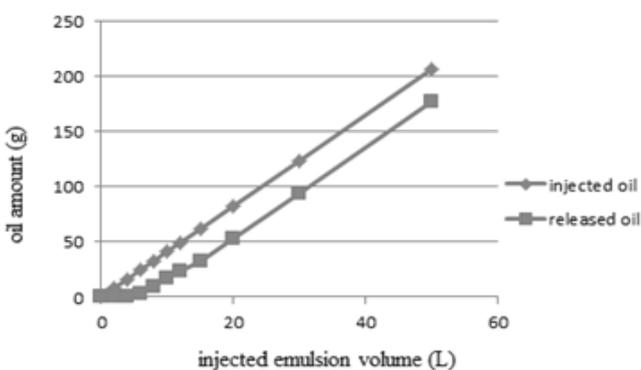


Fig.7. Oil in water emulsion percolation through filter bed (T=25°C, D=50ml/min)

dynamic responses of an adsorption column. Evaluation of the oil quantity in the effluent before and after percolation was tabulated in Table. 2.

When breakthrough occurred in the percolation system as shown in Fig.7, some quantity of oil was just introducing in to the effluent [18] The percolation of emulsion through PGAC is worked on the basis of following scheme showed in Fig 8.

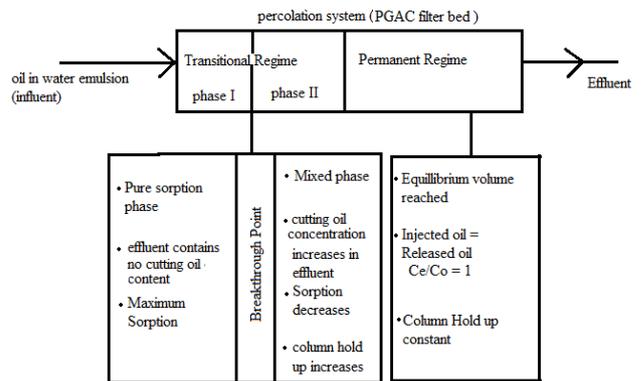


Fig. 8. Percolation of emulsion PGAC filter bed (column)

Under the mentioned operating conditions (oil in water emulsion conc.  $C_0= 0.5\%$ ,  $T= 25^\circ\text{C}$ , Flow rate  $D= 50\text{ml/min}$ ), the breakthrough volume and equilibrium volume were 3.8L and 14.5L respectively, therefore, the sorption capacity of PGAC was 7.3g/g and also confirmed by breakthrough curve shown in Fig. 9.

Table 2. Oil in water emulsion percolation through filter bed (column) at  $D= 50\text{ml/min}$ .

Effluent volume injected in filter bed (L)	Injected oil quantity(g)	Released oil content (g)	Hold up (g)
0	0	0	0
2	8.24	0	8.24
4	16.48	0.85	15.63
6	24.72	2.72	22
8	32.96	9.5	23.46
10	41.2	16.8	24.4
12	49.44	23.6	25.84
15	61.8	32.9	28.9
20	82.4	53	29.4
30	123.6	94.1	29.5
50	206	176.5	29.5

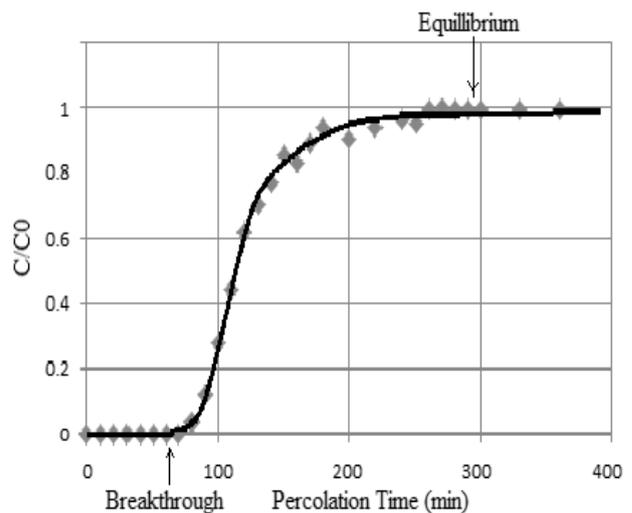
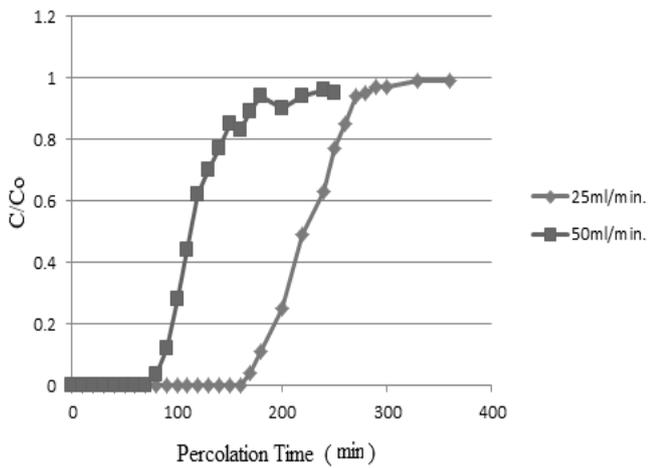


Fig.9. Breakthrough curve (T=25°C, D=50ml/min) of oil in water emulsion percolation system



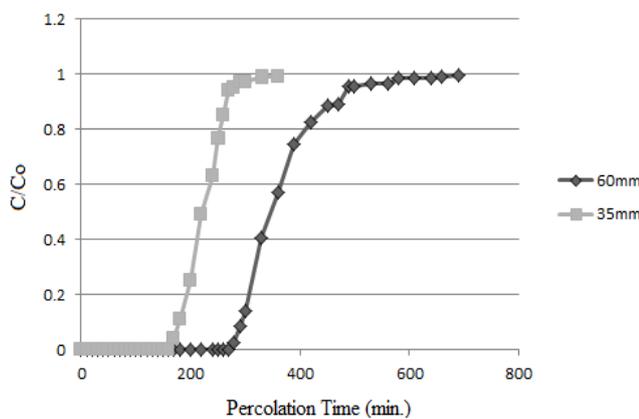
**Fig.10. Breakthrough curves (at  $T=25^{\circ}\text{C}$ ,  $C_0=0.5\%$  and  $H=35\text{mm}$ ) of oil in water emulsion percolation system with different flow rates**

*C. Sorption with varying flow rate (D)*

The influence of emulsion flow rate on the sorption capacity of PGAC filter bed, at initial concentration  $C_0=0.5\%$  and bed height  $H=35\text{mm}$ , was followed by varying flow rate 25 and 50 ml/min. According to the experimental facts the percolation system (PGAC filter bed) showed better adsorption of oil from oil in water emulsion at low flow rate (Fig. 10), because of longer residence time of emulsion in the filter bed, which enhances the possibility of coalescence between oil droplets and their entrapping in the filter bed. Breakthrough also occurs at longer time with lower flow rate due to less diffusion or mass transfer coefficient.

*D. Sorption with varying bed mass [height (H)]*

At influent concentration of 0.5% and flow rate of 25ml/min were maintained, the bed height of percolation system was varied as 35mm and 60mm to study its influence on breakthrough. As shown in Fig. 11, when the bed height is increased from 35 to 60 mm which is directly related to the amount of PGAC in percolation system, the breakthrough point takes longer time to occur. At increased bed height, there is increased reaction area and contact time between oil and sorbent.

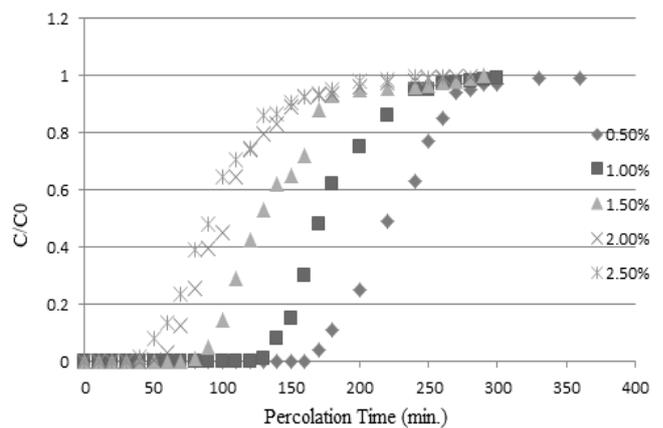


**Fig. 11. Breakthrough curves (at  $T=25^{\circ}\text{C}$ ,  $C_0=0.5\%$  and  $D=25\text{ml/min}$ ) of oil in water emulsion percolation system with different bed height**

Oil droplets coalesce each other to a large one and retention of oil occurs in inter fiber cavities, which resulted to treat a larger volume of emulsion and increased adsorption capacity of filter bed. Most of the studies have been reported the similar trend [19, 20]

*F. Sorption with varying influent concentration  $C_0$*

The effect of varying initial concentration  $C_0$  from 0.5% to 2.5% oil in water emulsion on adsorption capacity of PGAC at fixed height of filter bed  $H=35\text{mm}$  and flow rate  $D=25\text{ml/min}$  were studied by breakthrough curves presented in Fig.12. It was observed that breakthrough occur earlier at higher concentration and subsequent curves are formed at decreasing concentrations. There was more oil quantity present in 2.5% of influent concentration and maximum sorption occurs earlier in phase I of transitional regime, therefore, breakthrough occurred earlier than other breakthroughs of decreasing concentration. The presence of more oil molecules at higher concentration created a competitive field for fewer binding sites of the adsorbent which results the reduced adsorption capacity of PGAC at higher concentration.



**Fig.12. Breakthrough curves (at  $T=25^{\circ}\text{C}$ ,  $D=25\text{ml/min}$  and  $H=35\text{mm}$ ) of oil in water emulsion percolation with different influent concentration**

*G. Sorption isotherm*

To study the sorption isotherm of the system, the cutting oil concentration  $C_0$  in emulsion was varied from 0.5% to 2.5% and the related sorption capacities (measured at equilibrium), were quantified. Oil sorption isotherms were fitted to Freundlich equation. The sorption isotherm represent the relationship of the amount of cutting oil adsorbed by a unit weight of PGAC sorbent and the concentration of effluent at the equilibrium [21] Fig. 13 showed a better fitness with Freundlich isotherm model. The Freundlich parameter  $K_F$  represents the adsorption capacity and  $n$  predict the nature of sorption or sorption intensity. The system would be more heterogeneous as the value of  $n$  more closely to zero [22] As  $n$  value of this system was calculated as 1.77, the system may be assumed heterogeneous. If  $n<1$  indicates unfavorable sorption intensity [23] whereas Table. 3 showed favorable sorption intensity of PGAC which also makes it suitable for Freundlich isotherm.

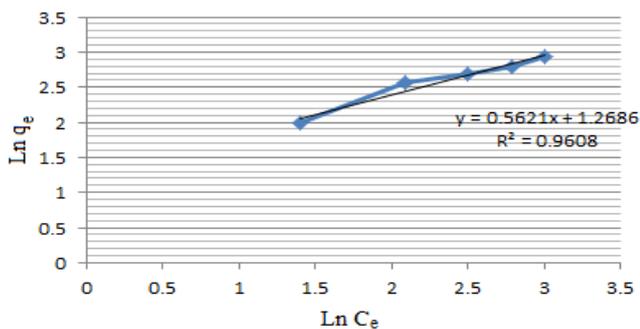


Fig.13. Freundlich isotherm for cutting oil sorption using PGAC at 25°C

Table.3. Sorption isotherm parameters of Freundlich model for the adsorption of metal cutting oil on PGAC and compared with other adsorbent

Freundlich Parameters	PGAC	MgO.CaO
$K_F$ (g/g)(L/g)	3.555	1.21
N	1.77	1.5625
$r^2$	0.9608	0.998

#### IV. CONCLUSION

The results obtained in this study showed that activated carbon prepared from agricultural waste material pomegranate peel may be used as a potential biosorbent for the removal of waste metal cutting oil from machining waste water efficiently. Some studies have been done on PGAC used as efficient adsorbent for heavy metal ions while present study introduced the Pomegranate peel activated carbon as better adsorbent for removal of metal cutting oil and showed prominent results in comparison to other well studied adsorbent e.g. CaO-MgO and walnut shell activated carbon. In continuous process more than 95% removal of MCFs occurred for 0.5% of influent concentration of MCFs. The investigations for efficient removal of high concentration of waste metal cutting fluid must be needed for overcome the significant proportion of water pollution.

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