Comparative sorption efficiency study through continuous flow method for machining waste water

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Abstract— Present study focused on the sorption capacity of self-prepared activated carbon from agro-based waste materials for the metal cutting oil removal from machining waste water. All the three adsorbents PGAC, PSAC and DMAC were prepared by chemical activation of waste materials such as Pomegranate peel, pumpkin seed waste and de-oiled mustard cake respectively. Each sorption process was carried out in a continuous sorption system. Governing factors for sorption of MCFs were proposed, analyzed and compared. The governing factors are the height of adsorbent bed, flow rate of influent, influent concentration and pH value of influent. A comparison was made between all the three prepared adsorbents on the basis of breakthrough curves. The breakthrough curve shows that PGAC has higher saturation percentage in comparison to the PSAC and DMAC. The effect of pH was also studied between 2 and 11. The results show that the removal of MCFs from influent was high at pH 7-9 for each adsorbent.

Index Terms— MCFs, PGAC, PSAC, DMAC, Saturation %.

I. INTRODUCTION

Air, water and soil are the three main requirements to survive their life for living creatures, in which water is one of the most prominent factor. But the scarcity of pure water is a challenging problem of today. It becomes very impossible to get pure water for living beings due to waste secretions from household and industries. Industrial wastewater exhibits inorganic and organic both type of pollutants in which emulsified oil has left an undesirable impact on the environment. Metal cutting fluids in the form of emulsified oil have the major contribution in waste water pollution. 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 consists a suspension of oil droplets in water, stabilized by surfactants, and usually contain several compounds such as biocides, de-foamers, rust inhibitors, anti-wear agent etc. [1]. Most of the waste metal cutting fluids in industrial waste water is non-degradable and toxic in nature. Therefore, industrial waste water must be treated before its disposal.

Till date, among many treatment technologies, the best available technology is adsorption on activated carbon due to its high efficiency and ability to separate wide range of organic/inorganic chemicals from water way stream [2, 3]. Many researchers have been focused on the use of solid waste, cheap and abundant natural product such as MgO – CaO, sawdust [4], walnut shell [5] and mango rinds [6] as adsorbents. Most of the reported studies on the adsorption of emulsified oil by activated carbon were conducted in batch studies [7]. We have focused our study on the use of agro based waste materials for the production of activated carbon. The adsorption study was done with these adsorbents in a continuous mode. We have used pomegranate peel waste, pumpkin seed waste and de-oiled mustard cake for the production of activated carbon. These can be used efficiently in removal of waste metal cutting fluids from industrial/machining wastewater at studied operating conditions. In the present study, we are going to compare the metal cutting oil removal efficiency of all the three adsorbents on the basis of % saturation factor and also with the other used adsorbent.

II. EXPERIMENTAL SECTION

A. Adsorbent Preparation

The various agro-based waste materials such as Pomegranate peel, Pumpkin seed waste and de-oiled mustard cake were collected from local market. It was cut into small pieces and manually de-hulled. These materials were washed with distilled water continuously and then with deionized water for removal of dirt particles and soluble biomolecules. After thoroughly washing materials were dried in sunlight until the moisture was partially evaporated and was further dried in hot air oven at 70-100°C for 24h until the residual moisture was completely evaporated showed constant weight. The activated carbon of these agro based waste materials were produced by using the method reported elsewhere [8]. The dried materials were grounded to a fine powder and made homogeneous through 90-300μm sieve and carefully labelled as PGP, PSW and DMC for Pomegranate peel, Pumpkin seed waste and Deoiled mustard cake respectively. The dried PGP, PSW and DMC were treated with concentrated H_2SO_4 or H_3PO_4 acid in the ratio 1: 2.8 by weight and kept in an air oven at 1 85°±5℃ 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℃ for 7-8h up to a constant weight and labelled as Pomegranate peel activated carbon (PGAC) [9], Pumpkin seed activated carbon (PSAC) [10] and De-oiled mustard cake activated carbon (DMAC) [11] for further sorption process.

B. Adsorbate Preparation

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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 30ºC measured with pycnometer and ASTM D445 respectively.

C. 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 each adsorbent were used in the experiment at which column have two different bed heights (H mm). 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 different flow rates (D). The effect of varying operating conditions such as flow rate, column/bed height, pH and influent concentrations on sorption capacity of adsorbents were studied by measuring the oil concentration in effluent as a function of time. The pH of influent (oil in water emulsion) was ranging from 2-11, which was adjusted by adding 1N HCL or 1N NaOH drops in the influent. pH was measured with the help of pH meter (Ecoscan).

Oil concentrations were determined by COD analysis, using reactor digestion method [12] on ELICO Double beam SL 210 UV Vis Spectrophotometer.

III. RESULT AND DISCUSSION

A. 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 metal cutting oil through column process has been described in terms of breakthrough curves for each adsorbent PGAC, PSAC and DMAC under varying operating conditions.

B. Sorption affected with pH of emulsion
The effect of pH value of prepared metal cutting fluid on sorption process was studied for each adsorbent PGAC, PSAC and DMAC with in the range 2-11. Figure shows the effect of pH at influent concentration (C_o) 1% for each adsorbent at 25°C. It is evident from the figure that sorption of MCFs was maximum with pH 8-9 and above pH 9 there was no considerable change occurred. The sorption of MCFs increased from 9.37 to 12.9 g/g (PGAC), 4.02 to 5.87g/g (PSAC) and 2.18 to 3.96g/g (DMAC) for an increase in pH from 6 to 11. It was found that oil sorption on organic sorbents was highly affected by pH value due to strong influence towards active groups (-NH-, -CO-, -CONH-, -CONH2-) on sorbent surface [13] and FTIR of each of adsorbent after adsorption showed the presence of these active groups on their surface.
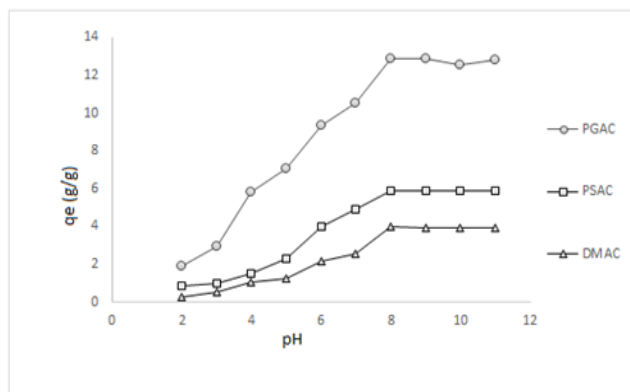

Fig 1. Effect of pH on sorption capacity of adsorbents PGAC, PSAC and DMAC at influent concentration C_o= 1% of metal cutting oil emulsion.

The increased adsorption with higher pH and decreased adsorption with smaller pH can be explained on the basis of H^+ ion concentration. At lower pH i.e. acidic pH, the H^+ ion concentration is higher which compete for adsorption sites at adsorbent results lower sorption occur.

C. Comparative study between all the three used adsorbents on the basis of breakthrough curves

The adsorption process was conducted in three columns at the same temperature T= 25ºC with the prepared adsorbents (PGAC, PSAC and DMAC). Each column was placed with different adsorbent at a same column length of 40mm and the oil water emulsion of concentration 1% was introduced in the column with flow rate of 35ml/min. at pH 8. The efficiency of each adsorbent was evaluated by determining breakthrough curves shown in Fig.2. The breakpoint C_b occurs when C/C_o=0.01 i.e. when the concentration of the effluent approaches 5% of initial concentration C_o. The volume of effluent passed through the column is V_b until the breakpoint reached and the column is called completely saturated when the concentration at exhaustion point C_x approaches C_o. The Primary adsorption zone (PAZ) is the part between C_b and C_x and the time required in formation of PAZ is t_x.
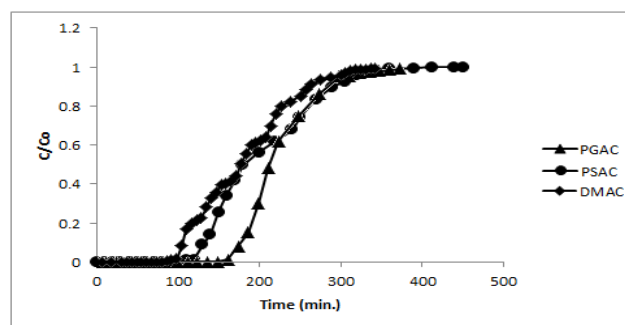

Fig. 2 Breakthrough curves of adsorption of metal cutting fluids onto the adsorbents (PGAC, PSAC, DMAC) at oil/water emulsion concentration Co=1%, column bed height H=40mm with emulsion flow rate D=35ml/min. at pH 8 and T=25ºC

According to Gupta et al.[14],

$$t_z = \frac{V_z}{F_m} \qquad (1)$$

F_m is the flow rate $\left(\frac{ml}{min}\right)$,

V_x is the exhaustion volume (ml)

The time required for movement of PAZ down the column is t_δ and calculated by:

$$t_\delta = \frac{V_x - V_b}{F_m} \qquad (2)$$

The relation between t_δ and time of formation of PAZ (t_f) is given by:

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} \qquad (3)$$

δ is the length of PAZ (cm), D is the depth of the adsorbent.

The relation between Fractional capacity of adsorbent and t_f is given by:

$$t_f = (1-F)\, t_\delta \qquad (4)$$

F is the fractional capacity of adsorbent in the adsorption zone characterized by removing the oil from emulsion under limiting conditions. F may also be represented as:

$$F = \frac{\int_{V_b}^{V_x} (C_o - C).dv}{C_o(V_x - V_b)} \qquad (5)$$

The saturation percentage in the column is presented by relation:

$$\%S = [1 - \{\delta(F-1)/D\}] \times 100 \qquad (6)$$

With the help of breakthrough curves (Fig. 2), the parameters t_x, t_δ, t_f, f and %S were calculated and tabulated in Table I.

Table I. Parameters used in formation of PAZ and saturation in the column of prepared adsorbent

Ad-sor bent	Tx min.	t_δ min.	t_f min.	f	δ cm	Saturation %
PGAC	300	172	19.09	0.889	2.4491	106.79
PSAC	440	328	-81.14	1.2474	2.5175	84.43
DMAC	305	203	-161.93	1.7977	1.7390	65.32

As shown in Table I, the time required for establishing the PAZ (t_x) is minimum for PGAC and maximum for PSAC. The time required for movement of PAZ (t_δ) is also minimum for PGAC and maximum for PSAC. The fractional capacities of the column (f) in the adsorption zone at the breakpoint are 0.889, 1.2474 and 1.7390 for PGAC, PSAC and DMAC respectively. The % saturation is in the order of PGAC>PSAC>DMAC, the given order reveals that the adsorbent PGAC has major percentage of saturation with a large adsorption zone while DMAC has less saturation percentage with small adsorption zone. These results disclose that the best percentage of oil removal occur with the use of adsorbent PGAC but the fractional adsorption capacity at breakthrough point is comparatively low than DMAC. But as Gupta et al., [15] argued that the adsorbent having smaller adsorption zone (δ) with higher fractional adsorption capacity (F) at breakpoint must exhibit best oil removal percentage. From this point of argument DMAC must be the better adsorbent than PGAC and PSAC with least % saturation and maximum fractional adsorption capacity (F) at breakpoint.

IV. CONCLUSION

The findings of the present work concludes that Pomegranate Peel, Pumpkin seed waste and 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 or conc. H_3PO_4. By comparing the characteristics of each activated carbon it can be concluded that pomegranate peel activated carbon (PGAC) will prove to be better adsorbent than other two. The pH of metal cutting fluid must be in between 7-9 for better adsorption on these adsorbents.

Table II. Comparison of removal efficiency between reported and present work

Sr.no.	Adsorbent	Adsorption Mode	Removal efficiency	References
1	Walnut shell Surfactant modified Barley Straw	Batch process	0.58g/g	[5]
2	Mango rind saw dust	Batch process	12.4-49.4 mg/g	[6]
3	Surfactant modified Barley Straw Banana Stem	Batch process	518.6mg/g	[16]
4	Banana Stem	Batch process	190mg/g	[17]
5	SDS modified chitosan	Batch process	2.5g/g	[18]
6	PGAC	Continuous process	7.3g/g	[9]
7	PSAC	Continuous process	5.876g/g	[10]
8	DMAC	Continuous process	3.965g/g	[11]

Because of using fixed bed continuous adsorption mode the removal efficiency of each adsorbent is better than the reported adsorbents (in Table II) which have been used Batch adsorption method for treatment of industrial waste water.

After survey of literature we can conclude that we have prepared a cost effective, easily industrial applicable, ecofriendly, agro-based waste manageable and most of all having better adsorption capacity for metal cutting fluids from machining waste water under continuous adsorption mode.

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