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Adsorption of Oil from Waste Water by Using Human Hair

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Abstract: The removal of oil from waste water using human hairs (gents & ladies hairs) was investigated in batch process. Column experiments were also done to evaluate the continuous removal of oil. In batch studies the behavior of the adsorption was investigated through studying the influences of pH, contact time and adsorbent doses. The oil removal rate increased with a decrease in pH. The maximum removal of oil achieved at pH 1.0 at 30^{o}C temperature. The maximum adsorption obtained from the batch process was 13.88 mg/g for gent's hair and 9.80 mg/g for ladies hair adsorbent. Langmuir and Freundlich isotherms were used to fit the equilibrium isotherm. Freundlich model is best suitable. The effect of bed heights (10 cm), flow rates (1 ml/min) and inlet oil concentration 15.2 g/lit on the breakthrough curve were studied using gents & ladies hair. The break through point has been observed after 60 min. for gents and ladies hair and exhaustion point observed after 300 min. for gents' hair and 270 min. for ladies hair.

Keywords: Adsorption, Human Hair, Isotherms, Kinetics

INTRODUCTION

Industrial growth has accelerated the emission of various oily wastes from the sources such as petrochemical and metallurgical industries. Transportation & domestic sewage. These oily wastes are one of the major pollutants of the aquatic environment. The special attention has been focused on the discharge of waste water & oily water & it regulatory restriction has become stricter. Oil water separation processes using polymeric or inorganic membranes have been proposed as effective & cost competitive alternative to conventional oil removal technologies but in present the commercial use of membrane in waste water treatment is currently limited by their low efficiency as well as high capital & operating cost. These problems of separation of oil from water are widely faced in the industries especially in petroleum industry effluent plants and in sewage treatment Industrial waste contains nearly 70% free oil. 25% emulsified oil & 5% soluble soil. Separation of oil from water is necessary of the following reason. Oil slick on surface of water can prevent oxygen transfer from atmosphere to water and lead to over low dissolved oxygen level due to microbial & oxidative attack on the hydrocarbon molecules. The Recycling of water it is necessary to remove oil because it may hinder the process.

- Oil in boiler feed causes foaming & so treatment is required.
- Oil & waxes solidify at low temperature & cause clogging in pipes & sewer line.
- Oil slick is responsible for the death of birds.
- The oil penetrates in the feathers there by affecting their insulation & buoyancy.
- Birds become colder & more susceptible to diseases & experience difficulty in floating & flying.

The paper uses elaborate techniques to purify contaminated areas in different environments after oil spills. Rather than discarding of the human hair it can be used to help cleanse the affected area, absorb the oil then utilized as an effective fuel derivation. The oil absorption of potential wasted hair fibers could produce valuable slot for our prevent & modern society. We have investigated the ability of the human hair to absorb a variety of potential hazardous oils. Including motor oils, bilge oils & crude oils that have the possibility of being spilled in terrestrial or aquatic environments. Current increased demand for refined crude oil products such as heating oils, lubricant oils, gasoline & jet fuel & other such related products necessitated transportation of rushing products over greater distances when environments any serious accident resulting in spills. We have tried different hair colors & feel that overall black gave the best results for adsorbing the most oil. We are also using hair pellets as fuel that can be help reduce global warming which has also been prevent to provide the cleanest burn of any solid fuel. Thousands of tons of human hair are cue everyday & thrown into landfills as a waste produces which no direct benefits. Hair is not an easily degradable substance these are instances of hair. Our project looked at the possibility of finding a use for waste hair could be used to clean up oil spills & that the oil could be recovered or converted in fuel pillets. Also, the separation results obey Frendlch's isotherm. Thus confirming that the oil removal is due to selective adsorption. As the process is ecofriendly and does not require any chemicals, it may lead to development of a new technique of separating oil water emulsion, which is simpler. The present work is inspired by a small note published in science Reporter, starting that NASA is on the job of trying to develop a technology that could do the separation of oil from water using human hair as an adsorbing medium. It is generally seen that hair has good adsorbing capacity for oils. Keeping this concept is mind, the subject is explored further and its application in the field of oil separation is studied. It is seen that at laboratory scale, the method is very efficient. Its efficiency is nearly 100% for free oil. However, the most intriguing thing observed is, its efficiency in separating emulsified oil. Since hair is very cheap and not easily biodegradable, the method may find a good usage for it.

MATERIALS AND METHODS

Preparation of adsorbent: The adsorbent materials used for the study were Gents and Ladies Hair. The hair sample was collected from saloon and beauty parlor. Materials were washed thoroughly with deionized water and also acid -alkali wash to remove the oily portion, oven dried at 60^{o}C for 24 hours .After drying the materials were kept in air tight plastic bottles. The waste water sample was collected from servicing center. The pH of the sample was adjusted with 0.1 N HNO_3 and NaOH solutions (APHA; 1998).

Methodology for separation of oil: Collect about 1 L of sample and mark sample level in bottle for later determination of sample volume. Acidify to pH 1 or lower; generally, 5 ml HCL is sufficient. Transfer to a separatory funnel. Carefully rinse sample bottle with 30 ml carbon tetrachloride and add solvent washings to separatory funnel. Preferably shake vigorously for 2 min. however, if it is suspected that a stable emulsion will form, shake gently for 5 to 10 min. Let layers separate, drain solvent layer through a funnel containing solvent moisture filter paper into a clean, tared distilling flask. Extract twice more than 30 ml solvent each but first rinse sample contain with each solvent portion. Combine extracts intared distilling flask with an additional 10 to 20 ml solvent. Distill solvent from distilling flask in a water bath at 70^o C. Place flask on a water bath at 70^o C for 15 min and draw air through it with an applied vacuum for the final 1 min. This method is known as partition-gravimetric method.

If the organic solvent is free of residue, the gain in weight of the tared distilling flask is mainly due to oil. Total gain in weight, A, of tared flask less calculated residue, B, from the solvent blank is the amount of oil in the sample.

$$\text{Mg/l of oil} = 100 \times (A-B)/\text{ml of sample}$$

Adsorption Isotherms: Adsorption isotherms demonstrate the relationship between equilibrium concentrations of adsorbate in the solid phase 'q' and in the liquid phase 'C' at a constant temperature. The adsorption isotherms are often obtained in the laboratory using batch tests in which the equilibrium data are attempted by various isotherms models. There are the initial experimental tests that determine feasibility of adsorption treatment. In attendance are many different isotherms models have been suggested for the adsorption of solutes in a liquid solution onto a solid surface. Langmuir isotherm is based on the assumption that point of valency exist on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule thus, the adsorbed layer will be one molecule thick. Furthermore it is assumed that all adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as follows.

$$qe = q_{max}\, b\, Ce/(1 + b\, Ce)$$

A linear expression for the Langmuir isotherm can be expressed as following.

$$\frac{1}{qe} = \left(\frac{1}{bq_{max}}\right)\left(\frac{1}{Ce}\right) + \left(\frac{1}{q_{max}}\right)$$

Where,

q_{max} = maximum metal uptake corresponding to the solution capacity (amount of metal ions per unit weight of bio sorbent to form a complete monolayer on the surface) (mg/g);

b = energy of adsorption (the ratio of adsorption / desorption rates) (1/mg);

qe = amount of metal adsorbed on the biomass (mg/g);

Ce = equilibrium (residual) metal concentration in solution (mg/l).

The constant q_{max} and b are the characteristics of the Langmuir isotherm and can be determined from Equation. A plot of 1/qe versus 1/Ce gives a straight line with a slope of ($1/b_{qmax}$) and an intercept of ($1/q_{max}$). The essential characteristics of Langmuir isotherms can be expressed in terms of dimensionless separation factor, R_L or r which describes the types of isotherms and defined by

$$R_L \text{ or } r = 1/(1 + b\, Ci)$$

Where b and Ce are the terms appearing in the Langmuir isotherms. The parameter indicates the shape of the isotherms accordingly,

R_L or r Value	Typesof Isotherm
r > 1	Unfavorable
r = 1	Linear
0 < r < 1	Favorable
r = 0	Irreversible

On other equation for isothermal adsorption, the Freundlich or van Bemmelen equation has been widely used for many years. This equation was based on the assumption that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm. The Freundlich equation has the general form

$$qe = K_f Ce^{1/n}$$

Where K_f and n are the constant and 1/n < 1, bond energies increases with the surface density. 1/n > 1, bond energies decreases with surface density. 1/n = 1, all surface sites are equivalent Frundlich equation can be put in a useful forms by taking log of both site.

$$\log qe = \log K_f + 1/n \log Ce$$

Thus, a plot of log qe and log Ce should yield a straight line for adsorption data which follow the Freundlich theory. The value of the constants n and k_f can be determine from the plot. The intercept, K_f, is roughly an indicator of sorption capacity and the slope, 1/n, is adsorption intensity. The Freundlich equation generally agrees quite well with the Langmuir equation and experimental data over moderate ranger of concentrations C.

Adsorption kinetics: The order of adsorbate-adsorbent interactions has been described using various kinetic models. Traditionally, the pseudo first order model derived by Lagergren finds wide application. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate equation of Lagergren:

$$dq_t/dt = K_{ad} (q_e - q_t)$$

Plot of log (qe – q_t) versus t gives a straight line for first order kinetics and the adsorption rate constant, K_{ad} is computed from the plot. Lagergren plot of log ($q_e - q_t$) versus agitation time t, for the present data is not linear. Hence, pseudo first order kinetics cannot describe the mechanism of oil – human hair interactions. On the other hand, several authors have shown that pseudo second order kinetics can describe these interactions very well in certain specific cases. The pseudo second order kinetics is given by:

$$dq_t/dt = K (q_e - q_t)^2$$

Rearranging the above equation, we get in the linear form

$$t/qt = 1/(Kq_e^2) + (1/q_e)\, t$$

If the pseudo second order kinetics is applicable, the plot of (t/qt) versus t gives a linear relationship that allows computation of q_e and K. The pseudo second order model which considers the rate-limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the adsorbate and the adsorbent is therefore applied.

RESULTS AND DISCUSSION

Effect of pH on the removal of oil: The effect of pH for the removal of oil was shown in fi.g.4.1. The role of hydrogen ion concentration was observed at different pH range of 1-9. Experiments were conducted at the initial oil concentration of 5340 mg/1 for gent's hair and 17650 mg/l for ladies hair, adsobent dose of 500 mg/50 ml and the contact time was 30 minutes. Results indicate that ladies hairs have the maximum adsorption capacity for oil removal than gent's hairs. The pH of the waste water sample is an important controlling parameter in the adsorption process. It is observed that the percentage removal of oil for gents and ladies hairs is higher at lower pH. The reason for better adsorption capacity observed at low pH values may be attributed to the large number of H+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of dichromate ions (Chand et al, 1994). In case of ladies hairs, at pH 1.0 the removal was found to be 87.98%which is much higher than that of gent's hairs at 77.90 % for the same pH.

Effect of contact time on the removal of oil: Experiments were carried out for studying the effect of contact time on the adsorption process by taking 50 ml of waste water sample containing oil with initial oil concentration of 3320 mg/l for ladies hair and 960 mg/l for gents hair with an adsorbent dose of 500 mg/50 ml and mixing for a predetermined time intervals of 10 mins and optimized pH of 1. From contact time data (Fig. 4.2) it may be seen that oil removal per unit weight of ladies hairs is very rapid than gents hair. The equilibrium time for the maximum removal of oil was attained at 60 minutes in case of ladies hairs and 70 minutes for gents' hairs.

Effect of adsorbent dose on the removal of oil: Effect of adsorbent dose of all adsorbent on the adsorption of oil in shown in figure no. 4.3 for all these case initial oil fixed at 10 mg/l and the amount of adsorbent dose was varied from 100-1250 mg for 50 ml sample. pH of the samples were adjusted to 1.0 for all adsorbent and optimized time also adjusted 60 min for ladies hairs and 70 min. for gents hairs. It has been observed that, with increase in adsorbent dose, the percent removal of oil also increase upto a certain level and beyond that more or less constant removal was observed. oil removal of 91.66% was observed with ladies hairs and 93.75% was observed for gents hairs at 500 gm/l of adsorbent dose at ambient temperature(30$\pm$1) and thereafter the percentage reduction was very small.

FIXED COLUMN TEST

Breakthrough curve is plotted between time and Ce/Ci. The initial concentration of oil in the solution minus the amount found in the effluent gave the amount of oil retained by the adsorbent. The process was continued till the effluent concentration of oil is near to initial concentration of oil. From figure 4.6 it is clear that initially percentage removal of oil was closer to 100% as the volume of effluent increases ratio of effluent concentration to influent concentration (Ce/Ci) also increases then it will remain constant for further volume of effluent, which gives the ultimate adsorption capacity of those adsorbents. The breakthrough curve shown in the figure was plot of dimensionless concentration (Ce/Ci) versus time (t). It was shown that breakthrough generally occurred more rapidly with faster flow rate. Breakthrough time reaching saturation was increased significantly with a decrease in the flow rate. In the foremost interval, the value of Ce/Ci increased quickly, the change then become slow. When at a low rate of influent, metal ions had more time to contact with a adsorbent that resulted in higher removal of metal ion in the column. While increasing in the flow rate, the results indicated that the adsorption capacity would reach the equilibrium value faster, which may cause a negative effect on the mass transferring efficiency of the metal ion. An increase in the rate of influent flow appears to increase the sharpness of the breakthrough curves. The curves exhibit a sharp leading edge and a very broad trailing edge, especially at high influent flow rates. The Broadness of the trailing edge is most likely due to slow intra particle diffusion within the pores of the immobilized biomass beads. Metal ions must first diffuse into the porous beads before sequestration of metal's ions by the biomass could take place. However the use of low flow rates will result in long overall processing times, which may not be desirable in practice when large volumes of solution have to be processed. It has been observed that, break through point comes after Ce/Ci=0.07 at 60 min for ladies hairs and Ce/Ci=0.04 at 60 min for gents hairs. Exhaustion point was observed after Ce/Ci=0.92 at 270 min for ladies hair and Ce/Ci=0.83 at 300 min for gents hair.

Adsorption isotherm study: The isotherm data obtained using both the Freundlich and the Langmuir adsorption isotherm models are shown in Table 1 and fig.6 to fig.9. On the basis of coefficient of correlation, the applicability of Langmuir and Freundlich isotherms were derived. For ladies and gents adsorbents the R^2 values of Freundlich plot are higher than Langmuir plot. The recommended isotherm equation for different adsorbent is selected on the basis of values of R^2. The linear equation of isotherm having more values of R^2 which is closer to 1.0 is the most effective fitting isotherm. Gents hairs were found to be the most effective adsorbents, as their values of coefficient of correlation 0.967 having maximum adsorption capacity of 13.88mg/g which are closer to 1.0 than ladies hair. Also the separation factor or equilibrium constant R_L, which is defined as R_L = l/ (l+bCi), where Ci is initial concentration of oil and b is Langmuir constant which indicates the nature of adsorption) the values of R_L. Presented in **Table 5.1**, indicate that the adsorption of oil for all the adsorbents is a favorable process as R_L values lie between 0 & 1.

Table-5.1: Recommended equation to different adsorbents

S. n.	Adsorbent	Langmuir parameter				Freundlich parameter			Recommend -ed Isotherm
		q_{max} mg/g	b l/mg	R^2	Separation factor R_L	1/n	K_f	R^2	
1	Ladies hair	9.8	0.023	0.753	0.027	4.25	4.57	0.931	Freundlich
2	Gents hair	13.88	0.55	0.913	0.005	24.39	11.03	0.967	Freundlich

Table-2: Kinetic equation and regression data for the adsorption of Cr (VI) on different materials

Sr. No.	Adsorbent (adsorbate)	Equation of graph	R^2
1	Ladies hair	$t/q_t = 0.1237\ t + 48.428$	0.803
2	Gents hair	$t/q_t = 0.086\ t + 21.10$	0.840

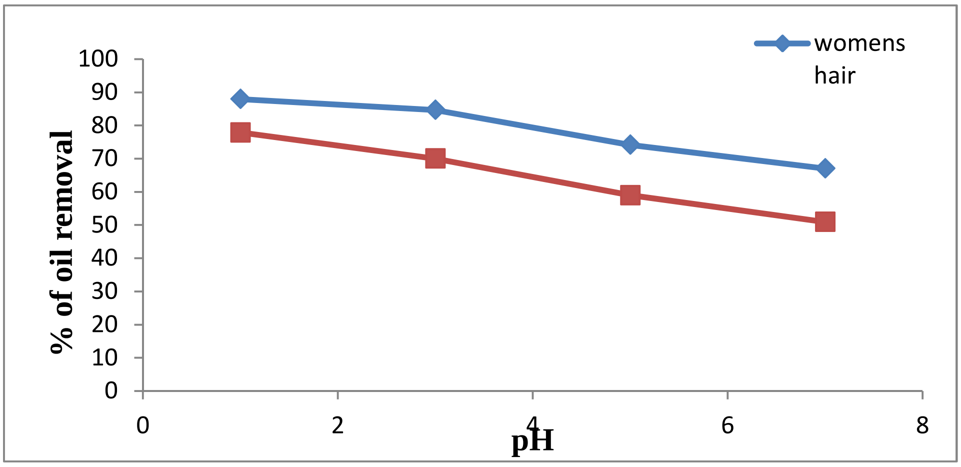

Fig. 4.1: Effect of pH on removal of oil by using adsorbent

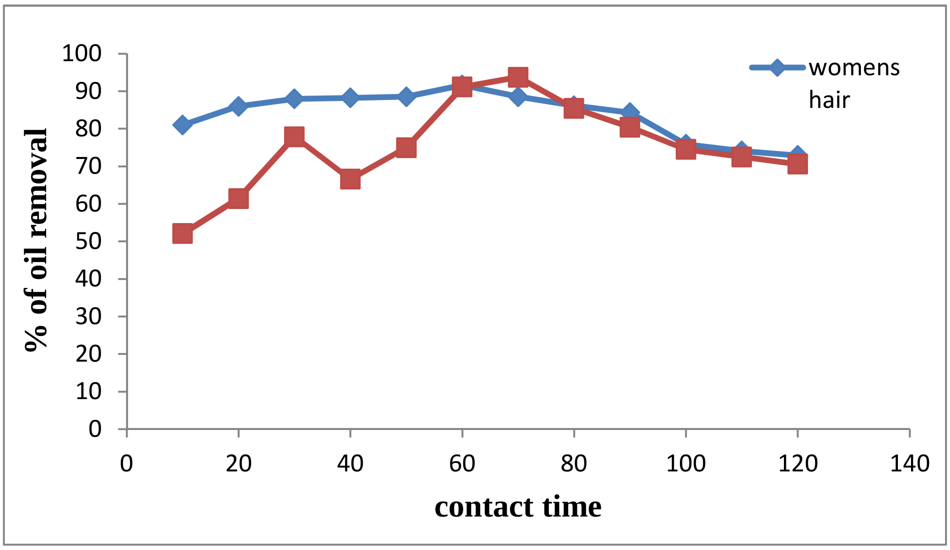

Fig. 4.2: Effect of contact time on removal of oil by using adsorbent

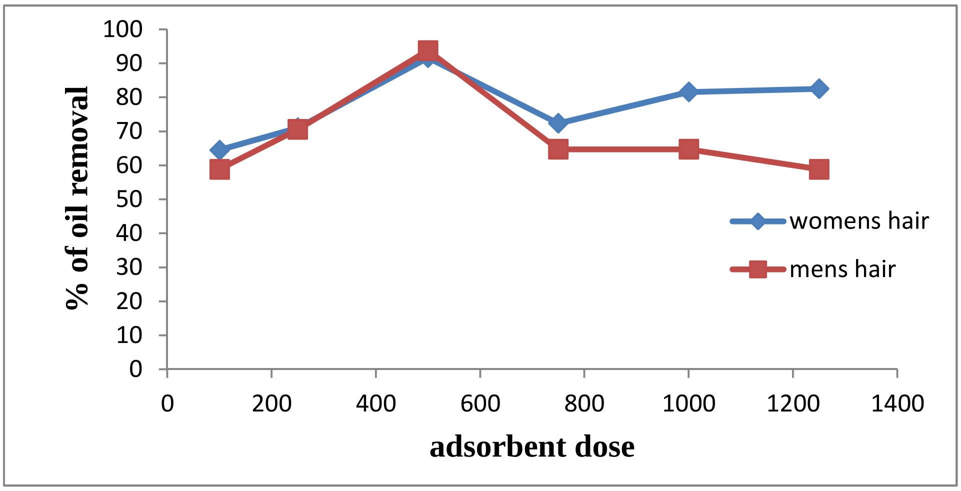

Fig.4.3: Effect of adsorbent dose on removal of oil by using adsorbent

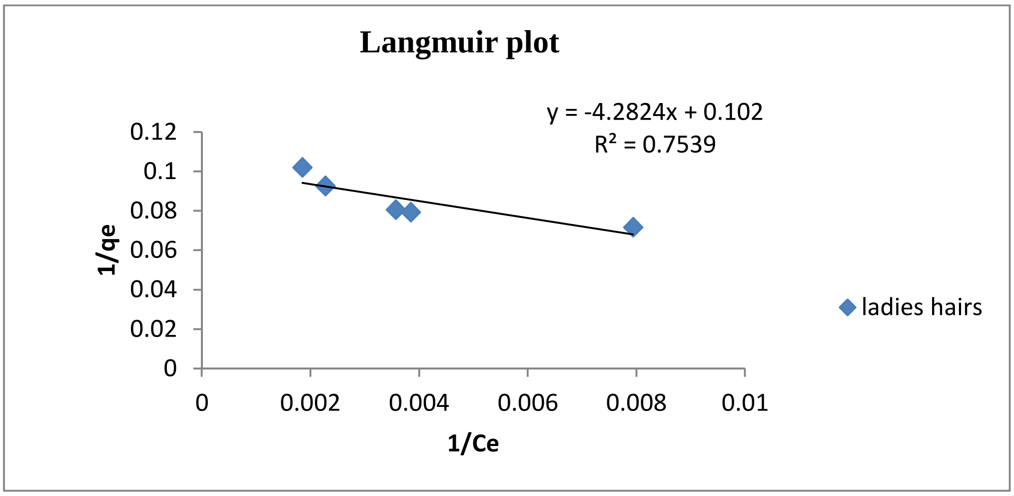

Fig.4.4: Langmuir plot for ladies hair

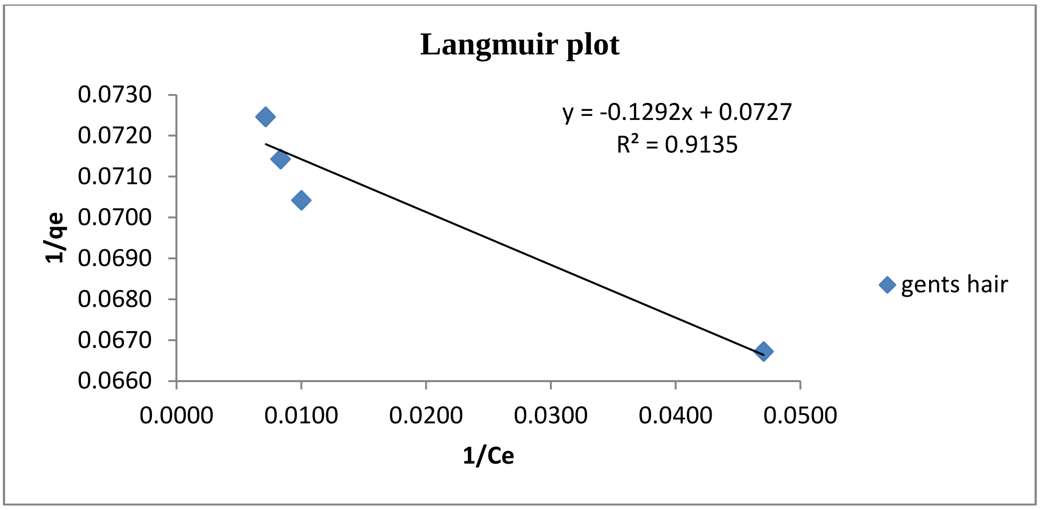

Fig.4.5: Langmuir plot for gent's hair

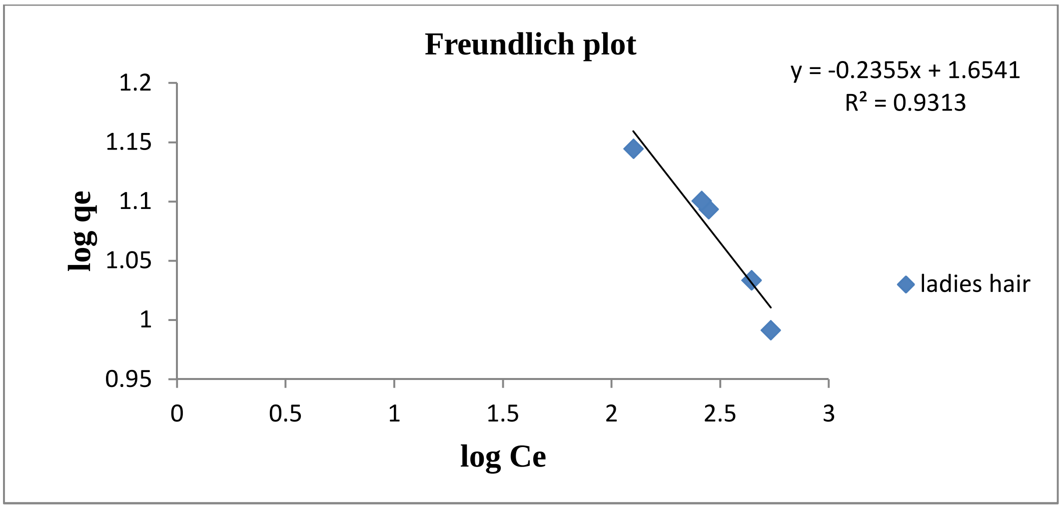

Fig.4.6: Freundlich plot for ladies hair

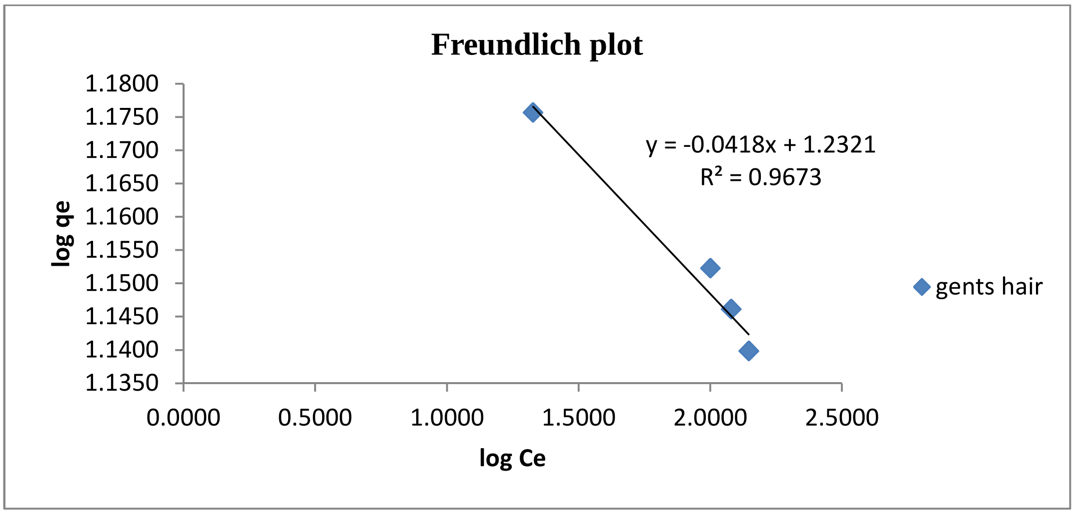

Fig.4.7: Freundlich plot for gent's hair

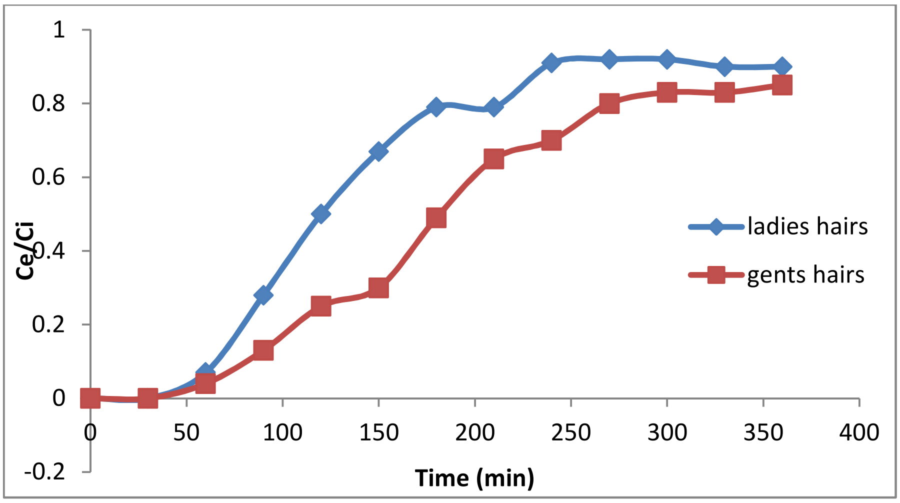

Fig.4.8: Break through curve

CONCLUSION

The adsorption of oil from waste water sample has been investigated on *ladies hairs and gent's hairs*. Parameters were studies in Batch mode process such as pH, contact time, adsobent dose. The optimum pH for the oil adsorption was 1.0 for *ladies hairs and gent's hairs* at 30±1^{o} C constant temperature. The results were verified by Langmuir and Freundlich adsorption models, and it was found that the results follow a Freundlich adsorption model.

The oil containing waste water sample was studied in a fixed down flow column process. Optimized parameter was taken from batch process. The adsorption capacity in strongly depends on the flow rate and bed height. As the flow rate was constant, the break through curve becomes sharper and break point time and adsorbed oil concentration dropped off.

From above discussion following conclusions to be justified,

- Human hairs are low cost adsorbent and can be used as best adsorbent for the removal of oil from waste water.
- Gents hairs showed better performance next to ladies hairs for the process of oil removal from waste water.
- Ladies hairs and Gents hairs followed Freundlich adsorption isotherm.
- At the optimized pH 1.0 with the adsorbent dose of 500mg/l and at the contact time of 70 min, the gent's hairs were effective in removal of 93.75% of oil from waste water than ladies hairs (91.66%).
- The result of the investigations is quite useful in developing an appropriate technology for the removal of oil from waste water by using human hairs.
- Regeneration studies are not conducted with a view that the cost of these adsorbents is very low; regeneration requires costly chemicals for the treatment of exhausted adsorbents.
- By using low cost adsorbents we can minimize the cost, instead of using costly chemicals or adsorbents. Low cost adsorbents improve the treatment process without affecting chemical characteristics of waste water
- As the flow rate is constant at 1mg/min, the break through curve become sharper. The break point time is obtained earlier and effluent adsorbate concentration ratio increase more rapidly

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