Use of Neem Leaves for Oil Removal from Waste Water

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Abstract

Adsorption is a well- recognized technique for treatment of wastewater streams containing petroleum effluents. The study undertaken aims to study the possibility of Neem leaves to be used as an effective biosorbents for the removal of oil from oil-water mixture. Neem leaves as biosorbents were employed to treat oily waste streams. The effects of biosorbent dosage, contact time and pH were evaluated. The optimal parameters were determined to be 2 g/L biosorbent dosage, pH 10 and equilibrium time of one hour. The adsorption of crude oil on Neem leaves powder (NLP) was best described by Langmuir isotherm and crude oil adsorption kinetics was determined to follow pseudo-second-order reaction kinetics. At optimal parameters, NLP was able to reduce crude oil concentration in tap water below the detectable limit, strongly suggesting the use of NLP as alternative to other adsorbents for oil-water emulsion treatments.

Keywords: biosorbent, produced water, oil-in-water, neem leaves

1. Introduction

The world today, in the era of modern technology, still depends chiefly on natural resources for energy requirements and Arabian Gulf area contributes a lot to fulfil the energy demands of the world. During the exploration of mining effluents, we not only obtain valuable high energy products of our concern but also huge amounts of undesirable produced (PW) water as byproduct [1,2]. Produced water having salinity more than sea water in most cases has diversified composition constituting treating chemicals, heavy metals, microorganisms, dissolved and dispersed oils, grease, radionuclides, salts, waxes, dissolved oxygen and numerous other dissolved gases [1, 3-5].

The highly contaminated and intoxicated produced water not only creates environmental pollution but also plays havoc to organisms' health by affecting digestive, respiratory and cardiovascular systems thus making it unsuitable to fall in the category of EPA standards for consumable water under the regulations of Pakistan as well as other environmental agencies [6-10].The amount of produced water depending upon the well operation time becomes equivalent to almost 80% of the total oil field volume [2, 11-13] .

Keeping in view the environmental and health hazards as well as prospect of beneficial uses, various techniques such as coagulation, filtration flocculation, de emulsification, flotation, destabilization by chemical additives and adsorption are employed to remove oil from PW [14-23]. Among these, adsorption being a physiochemical process is considered to be the most effective way in effluent treatment regarding cost, health and environmental issues [24-29].

Biological, physical and chemical techniques have been taken into consideration to treat PW but biological procedures employing naturally abundant biosorbents are always preferred because of being result oriented, cheap, easy availability and environment friendly benefits [30]. The traditionally employed adsorbent is activated carbon which is used to lessen the trace pollutants but its application is limited because of its higher initial and regeneration costs [1, 29]. Therefore, the development of adsorbent in terms of cost effectiveness is now the major area of concern and to tackle this burning issue numerous adsorbents have been examined to lower the oil amounts from PW to a minimum level. A wide variety of naturally available adsorbents provide plausible results including banana peels [31], pomegranate peels [32], eggshells [33], surface modified ball media fibers [34] , and modified barely straw [35].

Neem leaf powder has shown high efficacy for the removal of heavy metal ions from waste water [36,37]. Thus the studies on its adsorptive capacity make it acceptable to be used as biosorbent to decrease the traces of oil from produced water.

Neem (Azadirachta Indica) tree native to Assam, Burma and Indo-Pak and also widely spread in Sri Lanka, Bangladesh, Pakistan and Nepal is evergreen tree and grows enormously in tropical as well as in semi tropical areas [38]. The neem tree can grow even in drastically unfavorable conditions which ensure its growth in almost every part of the world. Its versatile medicinal usage as antibacterial, antifungal, contraceptive, sedative and antiviral makes it a wonder leaf [38-40]. A long life span and being naturally abundant all over the world neem leaves can be used reliably as biosorbents for oil removal from produced water [38].

In this article neem leaf powder is put under consideration to be used as a biological sorbent for crude oil removal from PW. The feasible operation conditions are evaluated. In addition to these the possible adsorption isotherms and kinetic parameters are studied.

2. Experimentation

2.1. Materials and Instruments

The neem leaves were collected from Multan (Pakistan) local territory neem plant while crude oil was collected from market. Analytical grade chemicals were used. Distilled water was prepared using water still (IM-50, IRMECO), Oven (ES100/G94, Tecnotest) was utilized for drying purposes. ARE Heating Magnetic Stirrer (F20520162, VELP Scientifica) was used to control temperature and stirring of mixture. pH was monitored by pH meter (HI 83141, Hanna instruments) and maintained using 0.1 M NaOH and 0.1 M HCl. Weighing balance (JJ523BD, G & G ®) was used for weight measurements. Particle size was reduced using grinder (BL9833-B, Enviro) and screening was done using Tyler Standard Screen Scale Testing Sieves (Van Waters & Rogers, Inc.)

2.2. Biosorbent and Produced Water Preparation

Fresh Neem leaves (NL) were washed using distilled water, air-dried for 24 hours, crushed to course particles and treated with n-hexane for two hours twice to remove colored pigments and soluble organic matter. Neem leaves powder (NLP) was then washed with distilled water dried at 70^oC, further grinded and sieved in already mentioned equipment. NLP was washed again with distilled water, dried at 70^oC in oven for 24 hour and then stored at room temperature in air tight glass containers [32,41].

Curde oil, having density 0.779 g/ml, was dispersed in tap water to synthesize produced water (oil dispersed in water mixture) in laboratory. Tap water instead of deionized or distilled water was preferred for oil-in-water mixtures (O/W) preparation [41,42].

2.3. Adsorption Experiments/Isotherms

Different dosage of biosorbent were added to known volumes of PW and stirred at a speed of 200 rpm for 2 hours at neutral pH and ambient temperature to determine the optimum dosage of NLP. After 2 hours, the NLP was separated from the mixture using Whattmann filter paper and the oil was quantified using n-Hexane as solvent in solvent-solvent extraction technique where the calibration curve for oil in n-Hexane was generated using absorbance of known concentrations of oil in n-Hexane. UV vis absorbance spectrometer was used to analyze the n-Hexane extract at wavelength of 300 nm. The same procedure was carried out to determine the optimum time by keeping the optimum dosage constant while optimum pH was determined keeping the dosage and time constant at optimum values. Temperature effects were studied keeping the dosage, time and pH at optimal values. Fig. 1 reflects the results for effects of NPL dosage on oil removal. Fig. 1 to 4 represents the optimum values of biosorbent dosage, time, pH and temperature at ambient temperatures. All the experiments, except temperature variation studies, were carried out at room temperature since the effect of temperature is quite pronounced in case of NLP as shown in Fig. 4.

3. Results and Discussion

3.1. Effect of dosage

At normal temperature, the dosage of biosorbent was varied from 0 to 5. Initially the removal efficiency of NLP increased appreciably by increasing the biosorbent concentration in the sample till 2 g/L after which it remained almost constant even at 5 g/L initial adsorbent dosage. The results clearly indicated 2 g/L to be the optimum dosage after which no consideration change in the removal efficiency of the NLP was observed.

3.2. Effect of contact time

The effect of contact time on the adsorption efficiency of NLP at normal temperature was analyzed by varying the time from 40 to 120 minutes, with an equal interval of 20 minutes. The adsorbent dosage was kept at 2 g/L and initial O/W concentration was kept at 200 mg/L. As shown in Fig. 2, the removal efficiency of NLP for 60 minutes was 78.67% after which no consideration change in removal efficiency was noticed. Keeping in view the constraints of time and energy, the equilibrium time of 60 minutes was selected and further experiments were carried out at the equilibrium time.

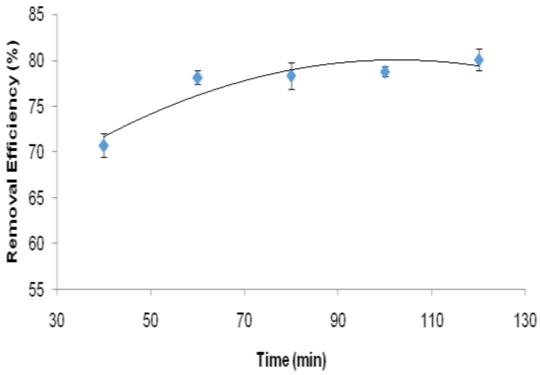

Fig. 1: Effect of biosorbent dosage on oil removal efficiency, adsorption parameters are 25°C, 7, 200 ppm, 2 hours for temperature, pH, initial oil concentration and stirring time respectively

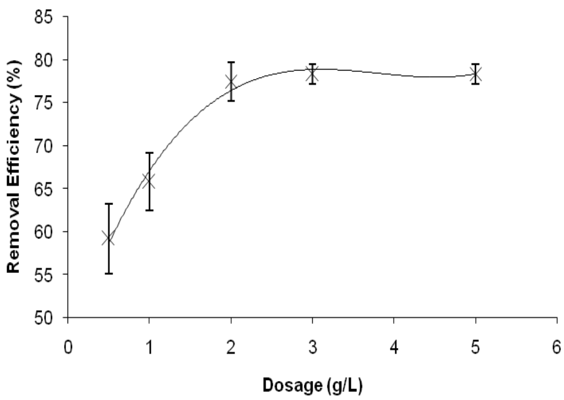

Fig. 2: Effect of contact time oil removal efficiency, adsorption parameters are 25°C, 7, 200 ppm, 2 g/L for temperature, pH, initial oil concentration and adsorbent dosage respectively

3.3. Effect of pH

The importance of pH in adsorption processes is implicit owing to its effect on biosorbent surface properties as well as on the available binding sites [43]. The oil removal efficiency of NLP at ambient temperature was investigated in this study which reveals that at lower pH the efficiency decreases while it increases as the mixture becomes more alkaline in nature The stirring speed, stirring time, dosage were 200 rpm, 60 minutes and 2 g/L respectively. At 5 pH the removal efficiency of NLP was calculated to be 70.87% which increased to 80.5 % at neutral conditions. The oil concentration in produced water samples was below detection limit for pH 10 and 12 which concludes that keeping other parameters at optimum values the oil can be successfully removed from O/W mixture using NLP. The decrease in removal efficiency in acidic medium can be attributed to the possibility that proton ion availability compete with the oil molecules in O/W mixture. The removal efficiency increases with increase in pH value that can be due to increase in hydrophobicity of NLP surface with increase in pH value and destabilization of O/W mixture at elevated pH [44, 45].

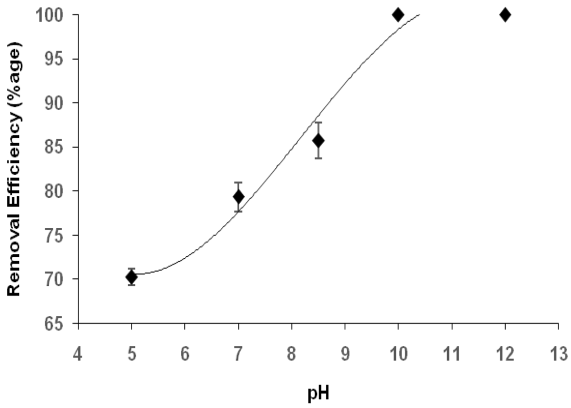

Fig. 3: Effect of pH on oil removal efficiency, adsorption parameters are 25oC, 60 min, 200 ppm, 2 g/L for temperature, stirring time, initial oil concentration and adsorbent dosage respectively

3.4. Effect of Temperature

The variations in the efficacy of sorption process by NLP are of prime importance owing to the pronounced change in the removal efficiency as temperature is changed. The adsorption process was carried out at 25 to 60 ^{o}C keeping adsorbent dosage at 2 g/L, stirring time of 60 minutes and pH at value of 10. The study of the experimental data presented in the form of graph (Fig. 4) suggests the process to be governed by exothermic process as the increase in temperature adversely affects the efficacy of the NLP to adsorb oil onto it. The trend of decrease in the sorption efficacy from 100 to 43 percent with an increase of temperature from 25 to 60^{o}C suggest 25^{o}C to be the best suited temperature for oil removal from O/W mixture using NLP.

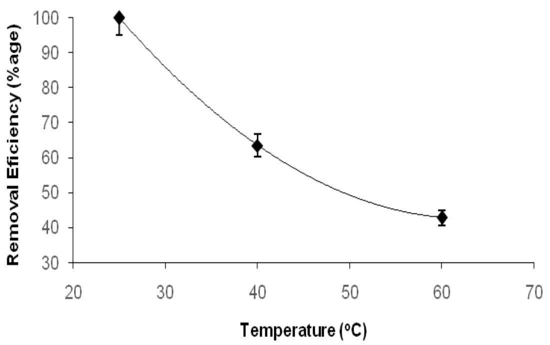

Fig. 4: Effect of temperature on oil removal efficiency, adsorption parameters are 10, 60 min, 200 ppm, 2 g/L for pH, stirring time, initial oil concentration and adsorbent dosage respectively

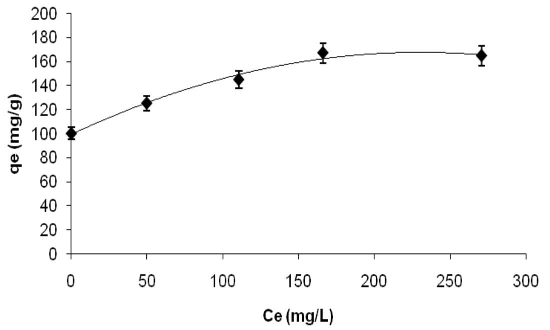

Fig. 5: Adsorption isotherms representing the amount of oil (in mg) adsorbed per gram of biosorbent in relation to the equilibrium concentration achieved. Adsorption parameters are 10, 60 min, 25oC, 2 g/L for pH, stirring time, initial temperature and adsorbent dosage respectively

3.5. Adsorption Isotherms

Study of adsorption equilibria is of prime significance to determine the sorption efficacy and sorption mechanism. The study of equilibrium sorption of oil at NLP surface at constant temperature was carried out at 25^{o}C, 2 g/L adsorbent dosage and pH of 10. The empirical relationships given by different isotherms are of utmost importance to determine the sorbate amount bound at surface and the amount present in the solution. The most commonly used isotherms are Freundlich and Langmuir [46]. However, the experimental data, in this study, was correlated using Freundlich, Langmuir, Dubinin-Radushkevich and Temkin adsorption isotherm models. The linearized form of Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin adsorption isotherm models are as follows, respectively

$$lnq_e = lnA_f + B_f lnC_e \tag{1}$$

$$\frac{C_e}{q_e} = \frac{1}{K_a q_c} + \frac{C_e}{q_c} \tag{2}$$

$$lnq_e = lnq_D - 2B_D RT(\frac{1+C_e}{C_e}) \tag{3}$$

$$q_e = BlnK_T + BlnC_e \tag{4}$$

where C_e represents equilibrium concentration, q_e is the equilibrium adsorbate amount adsorbed per gram of adsorbent, A_f and q_c represent the adsorption capacity while B_f and K_a represent the adsorption rate in case of Freundlich and Langmuir isotherm respectively. q_D, B_D are D-R isotherm constants. B and K_T are Temkin isotherm constants related to biosorbent where B represents the heat of adsorption.

These linearized plots were correlated with the experimental data, and the regression coefficient (R^2) of these generated plots gave values of 0.899, 0.993, 0.924 and 0.854 for Freundlich, Langmuir, Dubinin-Radushkevich and Temkin isotherms respectively. The Langmuir isotherm presents the best fitted model which points out the applicability of Langmuir isotherm in the present study. The Langmuir isotherm parameters q_c are K_a, as evaluated from the Langmuir isotherm plot, are 200 and 0.0892 respectively.

3.6. Adsorption Kinetics

In order to investigate biosorption mechanism and the rate-determining steps, kinetic models are exploited with the aim of selection for optimum conditions for large scale material removal processes. Several kinetic models have been published in literature, however, in case of biosorption the pseudo first order and pseudo second order kinetics are proclaimed to be most popular [47]. In this study, five kinetic models were correlated with the experimental data set. The linearized form of first order, pseudo first order, second order, pseudo second order and Elovich kinetic model is given by

$$\frac{1}{q} = \frac{1}{q_e} + \frac{K_I}{tq_e} \tag{5}$$

$$\ln(q_e - q) = -K_{PI}t + lnq_e \tag{6}$$

$$\frac{1}{C_e} = K_2 t + \frac{1}{C_h} \tag{7}$$

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{K_{2P}q_e^2} \tag{8}$$

$$q = \frac{1}{\alpha}\ln \alpha\beta + \frac{1}{\alpha}lnt \tag{9}$$

respectively, where q refers to absorbate amount at any time, C_h refers to highest initial concentration of solute, β is related to initial adsorption rate, α refers to energy of activation and surface coverage extent for chemisorptions while K_I, K_{II}, K_{PI} and K_{PII} is the rate constant for first order, second order, pseudo first order, pseudo second order reaction respectively.

The regression coefficients (R^2) of the above models were calculated from the plots to be 0.807, 0.856, 0.776, 0.998 and 0.709 in case of first order, pseudo first order, second order, pseudo second order and Elovich kinetic model respectively. The biosorption of oil onto NLP obeys pseudo second order reaction kinetics as only this model best fits the experimental data to an appreciable extent, Fig. 6.

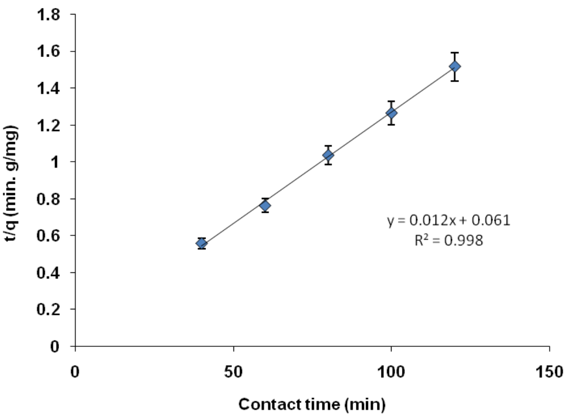

Fig. 6: Pseudo Second order Kinetic plot for NLP. Adsorption parameters are 10, 60 min, 25oC, 2 g/L for pH, stirring time, initial temperature and adsorbent dosage respectively

3.7. Regeneration and Desorption Studies

The used NLP was regenerated by n-Hexane. The procedure includes the use of 200 ml of n-Hexane to desorb any oil particles in the NLP at room temperature for 60 minutes. This regenerated NLP was used again at the optimum conditions determined before and the results displayed an average removal efficiency of 72%. The change in removal efficiency of NLP from its first use and subsequent use after regeneration is quite large; nevertheless 72% itself is quite efficient and regenerated NLP can be used to pre-treatment the waste water. Thus, being cheap and their ability to remove virtually all oil from the sample at room temperature, the NLP seems to be a promising biosorbent to treat waste oil-water streams industrially.

4. Conclusion

Neem leaf powder was employed as biosorbent for the treatment of waste water containing oil resulting in virtually complete removal of oil from produced water at normal temperature. The optimum factors were determined experimentally including dosage, time, pH and oil concentration in produced water. Five isotherms were tested and Langmuir isotherm was observed to give best fit with regression coefficient of 0.993. The NLP proved to follow pseudo second order kinetics having rate constant of 0.00236 g/mg.h. The results satisfactorily indicate the efficacy of NLP to be used as biosorbent for the oil removal from oily waste streams.

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