Removal of oil content in oilfield produced water using chemically modified kiwi peels as efficient low-cost adsorbent

Ali Saleh Jafer and Ali A. Hassan

Chemical engineering department, College of engineering, University of Al Muthanna, Al Muthanna, Iraq.

Email: alkhafajia31@gmail.com

Abstract: Adsorption was deliberate as a meaning of quantity of adsorbent and pH with contact time. It was found that the percentage of adsorption changed linearly with the quantity of dosage and time nonetheless varienon-linearly by pH. The Langmuir and Freundlich isotherm models were verified and adsorption was found in appropriate healthy into these models. The removal of oil content in oilfield produced water was inspected by kiwi peels. Kiwi peels were preserved with 0.1 M sodium hydroxide, followed by sulfuric acid with 0.1 M, and washed methodically. The got correlation coefficient (R²) for different dose optional suitable of the experimental data to Freundlich model for oil content in producing water. Results presented that modified kiwi peels were active and low-cost adsorbent can be productively rummage-sale for the elimination of oil content in produced water.

Keywords: Produced water, Oil removal, Adsorption; Adsorbents; Activated carbons; Low-cost adsorbents,

1. Introduction

Water is extensively secondhand in oil manufacture activities. Oil is originating subversive within obviously happening rocks together with assets of wastewater; this type of wastewater is identified as produced water (PW). The PW creates from two conceivable basics, which can be found under/overhead or privileged the hydrocarbon region or from injected liquids used in the crude oil withdrawal process, aromatic hydrocarbons, dispersed oil, and solvable organic compounds signify the composition of produced water [1,2], then are cleared into the environment directly or indirectly, attainment the water, air and food sources. These discharged organic are not recyclable and might experience alterations that have huge ecological, community health, and financial impacts [3-6]. The announcement of big amounts of contaminated produced water to the environment makes the essential for emerging and applying appropriate treatment skills, accomplished by eliminating harmful pollutants current in numerous of these industrial streams. These streams are difficult to luxury owing to large concentrations of oil content in produced water [7]. Altogether along extra severe ecological rules necessitate varied PW treatment after oil productions beforehand release and previously injection into reservoirs to decrease formation damage. Presently, appropriately treated produced water can be secondhand and rummage-sale for water flooding [8]. These helpful recycles directly reduces the
withdrawal of potable water, an extremely appreciated commodity in numerous areas of the biosphere [9 -11]. A variety of treatment technologies is obtainable with different degree of achievement to switch and lessen water contamination for instance: flotation [12], chemical oxidation [13 - 15] and membrane separation [16,17] . In the middle of numerous treatment skills, adsorption is a debauched and worldwide technique intended for treating organic compounds since of suitability, comfort of operation and ease of design [18, 19]. Yet; the expensive industrial cost brands conservative adsorbents for example activated carbon fewer frugally possible aimed at wide use in the treatment of produced water. The use of non-conventional, low-cost adsorbents prepared from agricultural wilds and spin-offs can not lone decrease a big amount of solid waste nonetheless to be actual attractive [20]. In the present investigation, the kiwi peels as environment approachable, lucrative, and obtainable locally. Kiwi peels as an adsorbent for the elimination of oil content in producing water solutions, which is extensively used in petroleum trades. Different limits effects such the adsorption dose, pH and contact time were shown in this education.

2. Materials and methods

2.1. Produced water

The produced water was obtained from the settling of the wet oil's unit, Ahdab oil field situated in Wasit -Iraq. It was collected in an environment alike to their native home that comprises oxygen till the treatment process is beneficial. The classification of PW is given in Table 1.

| Parameter                | value     |
|--------------------------|-----------|
| Oil                      | 110 (mg/L)|
| Turbidity                | 76.5 NTU  |
| pH                       | 6.35      |
| Dissolved oxygen content | 0.041 (mg/l)|
| Specific gravity         | 0.996     |
| conductivity             | 64520 μs/cm|
| TDS                      | 41292.8 (mg/L)|
| viscosity                | 1.101 m Pa/S|
| iron                     | 0.27 (mg/L)|
| sulphate                 | 45.6 (mg/L)|
| TSS                      | 15.6 (mg/L)|

2.2. Sorbent preparation

Kiwi peels (KW) were calm from native fruit fields in the southern portion of Iraqi and eroded with a watercourse of distilled water to eliminate grime, powder and any insincere scums. Kiwi peels were dried in sunlight for 85 hours and hydrolyzed with 0.1 M NaOH in dryer oven at 110 °C for 4 hours to constant heaviness. The pulp was eroded carefully with distilled water to eradicate lignin and pectin and dehydrated in oven at 110 °C for 24 h [21], 20 gm of KW was weighed in a spotless dry beaker of volume 500 ml. 100 ml of 0.1M sulfuric acid were additional to kiwi peels and the mixture was animated to 150–160 °C in 60min with infrequent stirring. The temperature was reserved in that range of temperature for 30 min. The subsequent black mixture was allowable to unruffled, and then filtered using filters paper (150 mm). The black consumed sulfuric acid was drinkable off and the carbonized substantial was eroded numerous times with distilled water and was stowed below dilute acidic circumstances (dilute sulfuric acid, pH 2 -2.5) to evade some bacterial growth [22]. The oil concentration in the PW was determined by means of a UV–spectra meter (UV-1800 Shimadzu, Japan) spectrophotometer associated with a PC at a maximum absorption wavelength (312 nm). The pH measurements were made with pH meter (Model 2906, Jenway Ltd, UK). The turbid meter (Lovibond, SN 10/1471, Germany) used to measure turbidity.
2.3. Biosorption process
The experiments of adsorption were conducted through measuring 100 ml of the PW taster and decanted hooked on a 250-ml conical flask. A total of 0.5 g of the adsorbent of KW was additional to the conical flask. The conical flask containing the adsorbent and the produced water was located on magnetic stirrer and surprised at 200 rpm at room temperature (25°C) aimed at a period of 90 min to safeguard equilibrium. The postponement was filtered, and the UV–spectra meter was used to examine the concentration of the oil content (OC) present in the PW. The adsorption capacity \( q_e (\text{mg/g}) \) subsequently equilibrium was intended using the following equation [23]:

\[
q_e = \frac{V(C_a - C_e)}{W}
\]

Where \( C_a \) and \( C_e \) are the total OC in produced water before and after adsorption and aimed at a period of time (ppm) correspondingly, and the volume of produced water used is signified by \( V \) (ml), whereas \( W \) signifies the mass (g) of the adsorbent. The percent oil removal was intended to use the following equation:

\[
\text{Adsorption} \% = \frac{C_a - C_e}{C_a} \times 100
\]

2.4. Test oil.
Previously analyzing a sample, the UV–spectra meter is adjusted using standard samples. Chief of all the standard tasters of identifying OC is prepared. By way of a preliminary point, we prepared a combination of 1 ml of oil in 9 ml of n-Hexane. This mother solution is diluted through numerous Capacity of n-Hexane to produce tasters by different oil concentrations. An appropriate volume (5 ml) of the extract is composed in spotless minicell cuvettes. The cuvette full with the excerpt is located in a cuvette adapter. The adapter hysteresis hooked on the taster compartment of the analyzer. The analyzer replies within 20 seconds.

3. Results and discussion
3.1. FTIR spectral analysis
The contrasts of the FTIR spectra of native kiwi peels were assumed in Fig. 1. The band at 3327.32-3007.12 cm\(^{-1}\) is \( O - H \) and \( C - O \) widening of polymeric mixes particularly polysaccharides (cellulose); 2928.04-2856.67 cm\(^{-1}\) intermission is symmetric shaking of \( \text{CH}_2 \) specifically alkenes, 1743.71-1681.98 cm\(^{-1}\) is stretching vibration of \( \text{COO}^- \), and 1656.91–1458.23 cm\(^{-1}\) band interval is bend shaking of \( C!4C \) (aromatic emaciated mode of lignin), 1458.23-1379.15 cm\(^{-1}\) is of phenolic \( O - H \) and \( C - O \) stretching of carboxylates, 1338.64–1240.27 cm\(^{-1}\) band interval is vibration of carboxylic acids, 1166.97–1087.89 cm\(^{-1}\) is vibration of \( C - O - C \) and \( O - H \) of polysaccharides, 1037.74–509.22 cm\(^{-1}\) band interval is \( C - H \) and \( C - C \) bend vibration and halogenated compounds’ \( (C - X) \) stretching vibration. FTIR spectra displayed that bark constituent was mainly compound of polymeric \( O - H \) collections, phenolic \( O - H \) and carboxylate groups and \( O - H \) groups of polysaccharides [24].
3.2. Effect of adsorbent dose and agitation speed

The percent adsorption and quantity adsorbed were augmented as the doses of adsorbent were augmented from 0.5 to 2 g at 110 ppm oil concentration on equilibrium time of 2 h. There was 56.8% elimination of oil content with 13.36 mg/g quantity adsorbed was experiential. Since Fig. 2 it is willingly tacit that the number of obtainable adsorption places and the surface area upsurge by cumulative the adsorbent dose, it consequently, results in the surge of the amount of adsorbed oil. After the formation of symmetry, it was experiential a reduction in quantity of adsorption. This might be credited to overlying or aggregation of adsorption places subsequent in a reduction in entire adsorbent surface area obtainable to produced water and by way of an upsurge in diffusion trail length. The agitating speed was diverse from 100 to 300 rpm, nonetheless from 200 rpm the consequences did not demonstrate any disparity, it leftovers constant with quantity adsorbed in addition to percent elimination of produced water [25].

![FTIR spectra of kiwi peels.](image)

![Effect of dosage on oil removal in 0.8 mm kiwi size.](image)
3.3 Effect of Contact Time

The consequence of contact time on the adsorption OC of produced water through the modified kiwi peels is exposed in Fig. 3. The adsorption is actual debauched firstly and formerly gradually reaches the adsorption equilibrium. This can be credited to huge free surface locations obtainable at an early stage of treatment time shadowed by less accessible places owing to disgusting forces between the oil content and adsorbent stages [26]. The majority of PW in adsorption equilibrium was attained in between 30 and 120 min for OC and the sorption tends to saturate at 120 min.

![Fig. 3. Effect of contact time on oil removal in 0.8 mm kiwi peels size, pH=6.35, room temperature.](image)

3.4. Effect of pH

Amongst all additional parameters, pH of the solution has been originated to be the greatest significant one. It not only affects the speciation of oil ions but then again to the charges on the sorption places of biomass sort. Consequently, it is very significant to reflect the ionic conditions of the useful groups of the bio-sorbent. Therefore the result of pH on the elimination competence of OC was deliberate at different pH ranging from 2.16 to 9.67 as shown in Fig. 4. It can be understood that adsorption of oil content was powerfully pH-dependent. The equilibrium acceptance of oil augmented notably with levitation the pH from 2.16 to 4.0. Overhead these levels, the capacity of adsorption did not change meaningfully equal to pH 9.67. Similar tendency was stated for adsorption of malachite green onto chemically modified rice husk [27].while higher pH reductions the quantity of positive H⁺ and upsurges the undesirable charge on the surface of the cross-linked terpolymer, foremost to higher electrostatic magnetism with oil ions [28].

![Fig. 4. Effect of pH on oil removal in 0.8 mm kiwi peels size, 1.5 g dosage, room temperature.](image)
3.5. Adsorption isotherm studies

The adsorption equilibrium data of oil content on KW were calculated by Langmuir and Freundlich isotherm models. The Langmuir model proposes a monolayer adsorption on a homogenous surface, and there was no communication between adsorbed species. The regression constant values were arbitrated to discovery the applicability of these models [29]. Produced water was rummage-sale for linear regression calculations. It is signified by the appearance below:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Where $C_e$ the equilibrium concentration (ppm) and $q_e$ is the quantity adsorbed per specified quantity of adsorbent (mg/g), $K_L$ is the Langmuir equilibrium constant and $b$ is the quantity of adsorbate obligatory to procedure a monolayer. Hereafter, a plot of $1/q$ against $1/C_e$ should be a straight line with a slope ($1/b$) and an intercept as $(1/bK_L)$ by way of exposed in Fig. 6. The Langmuir kind adsorption isotherm specifies surface homogeneity of the adsorbent and suggestion to the deduction that the surface of adsorbent is complete up of minor adsorption covers which are energetically equivalent to each other in admiration to adsorption marvel. The values of constants $K_L$ and $b$ were calculated and reported in Table 2.

![Langmuir isotherm plot for adsorption of oil content on produced water sample.](image)

**Table 2:** Isotherm parameters for produced water adsorbed onto kiwi peels samples obtained by using Langmuir model

| SAMPLE | B     | $K_L$  |
|--------|-------|--------|
| PW     | 0.193 | 27.05  |

The Freundlich isotherm model clarifies the interaction between adsorbate particles and adsorbents with multilayer adsorption on heterogeneous surfaces. Rendering to this model [30]:
\[ q_e = K_F C_e^{1/n} \]

Where \( K_F \) is Freundlich equilibrium constant, \( n \) is an experiential constant and break of the terms have the normal meaning. Therefore, a plot of \( \log q_e \) against \( \log C_e \) should be a straight line with a slope \( 1/n \) and an intercept of \( \log K_F \) as shown in Fig. 6. A plot of \( \log q_e \) against \( \log C_e \) stretches a straight line graph with \( (1/n) \) as the slope and \( \log K_F \) as the intercept. Both \( K_F \) and \( n \) determine the curving and the steepness of the isotherm.

Fig. 6. Freundlich isotherm plot for adsorption of oil content on produced water sample.

The appropriate of the data to the Langmuir and the Freundlich isotherms proposes that the biosorption of OC onto the biomass can be clarified by the isotherms, the Freundlich model clarifies the adsorption process better than the additional model on the foundation of the correlation factor \( R^2 \) (0.98). The highest bio-sorption capacity was found to be 13.36 mg/g, this trend is comparable to cases reported in the [31].

4. Conclusions

The results got from this effort exposed that kiwi peels are an active and low cost adsorbent for the elimination of oil content in produced water aqueous solutions. The adsorbent had respectable adsorption capacity for oil content and presented robust adsorption. Adsorption limits intended from Langmuir and Freundlich isotherms are valuable for the clarification of the mechanisms of the adsorption process in place of specified by the good linear correlation constant values. Adsorption capacity of kiwi peels is found to be similar to those of other agricultural waste materials hence kiwi peels might find manufacturing requests for the treatment of oilfield produced water containing organic content. The enhanced pH for oil elimination was found to be 3, adsorbent dose 1.5 g/L and contact time of 120 min. The adsorption of OC by kiwi peels was strongly dependent on pH, adsorbent dose and contact time. The oil elimination was maximum 90% at pH 2.16 in 1.5g kiwi peels with 150 min.
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