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Use of Natural Coagulants for Removal of COD, Oil and Turbidity from Produced Waters in the Petroleum Industry

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Abstract

The biggest amount of wastewater that produced from industry of petroleum is produced water, it contains suspended and dissolved solids, residual hydrocarbons, numerous organic species and heavy metals. It is very important to remove the organic pollutant compounds from the contaminated water before discharge into any natural water. This paper studies the effect of dose of natural coagulants, pH of produced water, and oil concentration on the removal of turbidity, COD and Oil from oilfield produced waters. The efficiency of turbidity, oil and COD removal was studied via three different natural coagulants (*Cicer arietinum* seed, eggplant seed and radish seed) used to decrease the turbidity and organic pollutants of produced water. The experiments of the jar test showed that *Cicer arietinum* seed at dose 1.5 mg/L and the best pH and oil concentration can remove 95.2% of chemical oxygen demand (COD), 83.8% oil content and 98.89% of turbidity. Also, the eggplant seed at optimum condition removed COD, turbidity, and oil content by 92.18%, 99.42%, and 81.8%, respectively from the produced water. Moreover, when radish seed was used, the removal of oil content, COD and turbidity will reach to 88.2%, 93.48%, and 98.78%, respectively.

Keywords: Coagulation; Flocculation; Natural coagulants; Turbidity; Oil; COD; Removal

Introduction

The industry of gas and oil deals with a huge amount of wastewater as a by-product to explore the gas and oil. This a massive quantity of wastewater represents a produced water and it increases when the operation time is well, and approximately that increase can reaches to 80% [1]. Due to discharge of produced water, the surface, soil and underground water may become very pollutant. The wastewater that produced from industry of Petroleum contains compounds: Inorganic and organic [2].

Colloid particles can be removed from wastewater by utilizing several traditional and advanced technologies, such as coagulation, flocculation, adsorption, ion exchange, flotation, membrane, precipitation, solvent extraction, biological, filtration and electrolytic methods [3]. Coagulation and flocculation treatment is among the methods available for water treatment, it is a simple, reliable, low cost and low energy consuming process that is commonly practiced [4]. It is an efficient method for treatment of water pollutant, and was used extensively for the treatment of different types of wastewaters such, as oily wastewater, pulp mill wastewater, sanitary landfill leachates, palm oil mill effluent, textile wastewater and others [5-8] because it did not require complex machineries; as well in the operation of process, no needs to consumption of energy, therefore we get the coagulant effective. It is an effective process to remove the colloid, soluble and suspended particles and also remove the other kinds of pollutants, such as organic compounds, color, micro pollutants, fat and oils during the aggregation that produced from macro and micro particulates into size of bigger ones followed by sedimentation [4].

In coagulation method, small particles are formed into larger aggregates (flocs). Dissolved organics matter will be adsorbed by these flocs. Larger particles are easier to remove by filtration or sedimentation. This process will reduce the dissolved organics matter and turbidity in liquids [9]. In general, there is a special definition for each of the term "coagulation and flocculation". Nevertheless, it was acceptable that referring for both processes as coagulation process in treatment of wastewater [10].

Coagulation includes the following stages:

(a) Coagulant forming;

(b) Particles destabilization; and

(c) Particles aggregation [11].

By adsorption, the particles and flocs have been aggregated by the natural coagulants and then followed by charge neutralization or bringing of particles. There are four mechanisms for coagulation to occur in the aggregation of particulates: (1) double layer compression; (2) sweep flocculation; (3) adsorption and charge neutralization; and (4) adsorption and inter particle bringing [9]. Therefore, coagulation is the process of destabilizing the colloids, suspended substances and other organic matter by adding coagulants to the liquids and allowing them to be converted into a bigger form that is easier to remove later. Different mechanisms, such as neutralization of charge, adsorption, and sweep flocculation can be responsible for the removal of organics particles and compounds depending on the concentration of coagulant and properties of water [12,13].

Aluminium and iron salts are the most commonly coagulants used to the treatment of wastewater [14]. However, aluminium could cause different types of bad effects on the health of human, e.g. memory loss, intestinal constipation, abdomen colic, spasms, difficultly of learn and loss of energy when utilized as a coagulant in the treatment of wastewater. Therefore, at present, there is a great interest in the improving and implementing of natural coagulant in pollutant water treatment [15]. The plants, animals and minerals are sources of natural

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coagulants. Natural coagulants that got from the plants are more common due to their suitability for large production and practicability for it. Natural coagulants are nontoxic, renewable, produce lower sludge, biodegradable and relatively cost effective [9,16,17]. Moreover, natural coagulants have a wide range of effective dosage and do not change the value of pH for treated water [9,18]. Therefore, the aim of present work is to study the use of natural coagulants in low concentration, such as *Cicer arietinum* seed, eggplant seed and radish seed which are locally available from vegetables for treatment the produced water. There are no any conducted experiments by the researchers for the treatment of produced water with using the seeds of eggplant and radishes, but some of them have used the *Cicer arietinum* at high concentration up to 50 mg/l, where there is no researcher has used low concentration up to 1.5 mg/L of the *Cicer arietinum* seed alone.

Research Methodology

Materials

In this research three various natural coagulants were utilized; *Cicer arietinum* seed, Eggplant seed and Radish seeds. All the coagulants used were provided by the local market.

Synthetic wastewater preparation: To prepare the synthetic produced water, some of chemical materials were added, such as clay materials, crude oil and salt to adjust properties of the produced water that treated in this research. The value of turbidity and oil of the synthetic water was set to become equal to the values of oil, turbidity and salt in the natural produced water. The clay materials and crude oil were added to the distilled water. The suspension was stirred for about 15 min at 2700 rpm to get a uniform diffusion of oil drops and clay particles.

Natural coagulants preparation: The seeds of radish and eggplant were collected and then dried naturally by sunlight. By using domestic blender, the dried seeds were ground to fine powder and then this powder was sieved through 600 μm sieve [19,20]. The size of granules powder should be less than 600 μm approximately to realize the solubility of active components in the seeds. Distilled water was added to the powder seed to get 1% suspension of it, and then shake vigorously for 45 min by using a stirrer to enhance the water for extracting the proteins of coagulant, and then passes through the paper of filtration. This filtrated solution was used as dose of coagulant in the experiments. To avoid any effect, such as changing in viscosity, coagulation activity and pH that occur, the solution should be papered daily and kept in refrigerator. Solution must be shaking well before using it.

Methods

The experimental methods that were used in the coagulation/flocculation treatment for wastewater were carried out by using jar test, which is most commonly. Samples of produced water that was used in the experiments was synthetic wastewater, the properties of the samples are shown in Table 1. Jar test was used to coagulate the samples of produced water by adding some coagulants in the experiment. All the experiments of coagulation – flocculation treatment were performed at the ambient temperature. The sample should be mixed well before using of the jar test and after that, the samples must be measured for oil, COD and turbidity to represent the initial concentration. 1liter of the produced water was put in beakers, then mixed at a high speed reaching to 150 rpm for 1 min by using a stirrer, and then mixed slowly at a speed of 50 rpm for 20 min, and finally the sample was left to settle for 15min. After settling the sample, a volume of liquor supernatant was pulled at a distance of 5 cm from the surface of the sample for conducting the analysis required. Coagulants of varying concentrations (0.5-3) ppm were added in the beakers to determine the best dosage based on the minimum concentration of pollutants. To determine the best value of pH, the experiments were carried out at the range of pH (2-11). Also, different concentrations of oil (50-1000) ppm were tested to find the best concentration of oil.

Results and Discussion

Determination of optimum doses of coagulants

Optimum dose for turbidity removal: Figure 1 shows the required optimum dose for various natural coagulants for reduction of turbidity. The removal efficiency of turbidity increases with increasing dose of natural coagulants until reaching the best removal at optimum dosage. The optimum dose for different coagulants in terms of turbidity removal is 1.5 mg/L *for Cicer arietinum* seed, 2 mg/L for eggplant and radish seed, and then the removal efficiency of turbidity decreased due to the overdose which caused restabilization of particle colloid. The performance of turbidity removal (98.68%) was high when using eggplant seed compared to other natural coagulants and approximately the same for radish seed and *Cicer arietinum* seed at optimum dose.

Optimum dose for oil content removal: Figure 2 indicates the impact of dosage of natural coagulants on the efficiency removal of oil. It is clear that the oil content decreases with increasing dose of natural coagulants until reaching the optimum dose. Furthermore, increasing the doses causes an increase in the oil content and a reduction in the removal efficiency, the overdose results destabilization, which leads to a weak attraction between the oil droplets and then causes a reduction in the settling velocity of particles according to the Stock law, thus the removal decreasing? The optimal dose of (1.5 mg/L) for all coagulants has a significant effect on the removal efficiency of oil it reached the best removal (86.9%) and residual oil (13.1 mg/L) by using radish seed.

Optimum dose for COD removal: The removal efficiency of COD by adding natural coagulants is shown in Figure 3. This figure reveals that the removal of COD increases with increasing the natural coagulants dose until the R% reaches the maximum value and then decreases. The performance of process treatment decreased the result for re-stabilization of colloids in wastewater that caused by the coagulant overdose. In addition, overdosing of coagulant would increase the formation of sludge overly; increase the chemicals and residuals management costs. The optimum dose could not neutralize the colloidal due to the quantity of coagulant that was not enough for this purpose. *Cicer arietinum* seed was the best in removal of COD and gave the ratio of removal reached up to (94.73%) and residual (132 mg/L) at the optimum dose 1.5 mg/L.

Determination of optimum pH

Another group of jar tests were carried out to evaluate the impact of pH on the efficiency removal of turbidity, oil and COD. Study the effect of pH on the effective process of coagulation is necessary because the solubility of particle and matters rely on the pH value of water. Figures 4, 5 and 6 depict the removal of turbidity, COD and Oil at different pH values (2- 11). According to these figures, it can be seen that the removal efficiency without prior adjustment of pH (7) was at the highest for all types of natural coagulants. Coagulation activity of natural coagulants in produced water becomes high at pH (7). The removal efficiency of pollutants decreased when the pH was higher than 7. This drop was due to the OH– ions concentration, that was high so enough to compete with organic molecules from the produced water for adsorption process. Also, when the value of pH was high the charge of the coagulants types would be less positive and as a result would become less attractive to the anionic organic compounds.

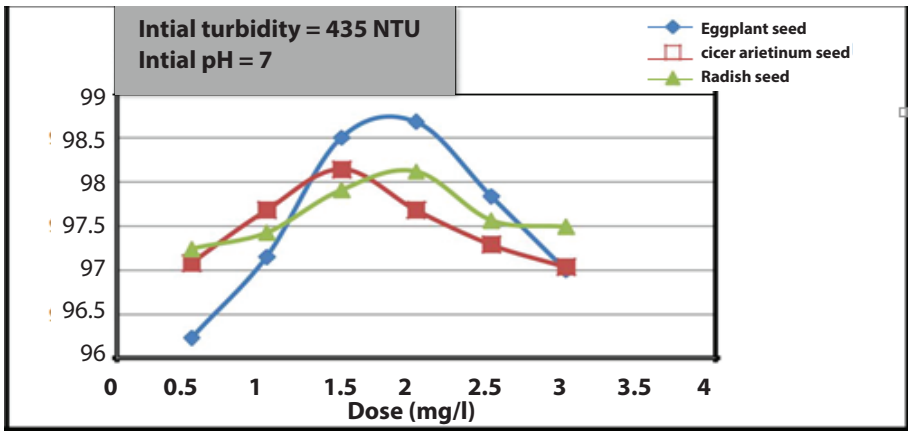

Figure 1: Effect of natural coagulants dose on turbidity removal.

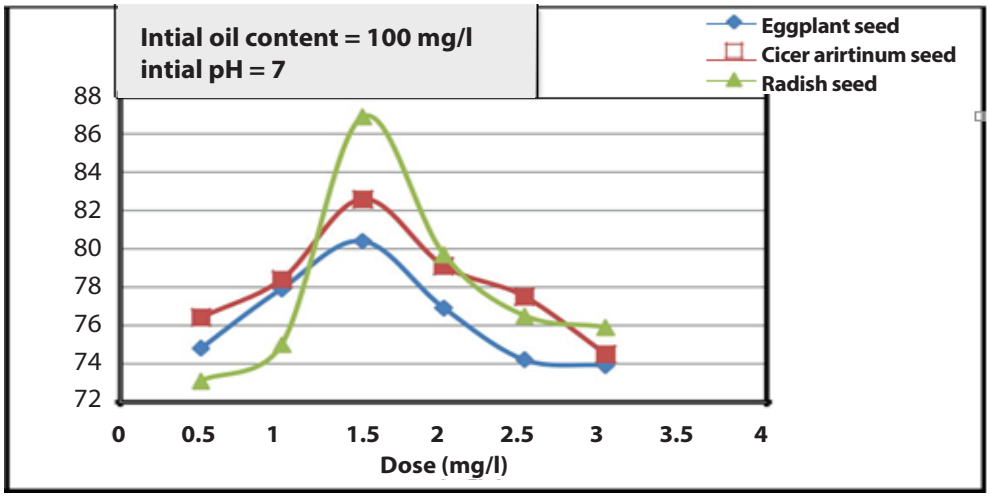

Figure 2: Effect of natural coagulants dose on oil removal.

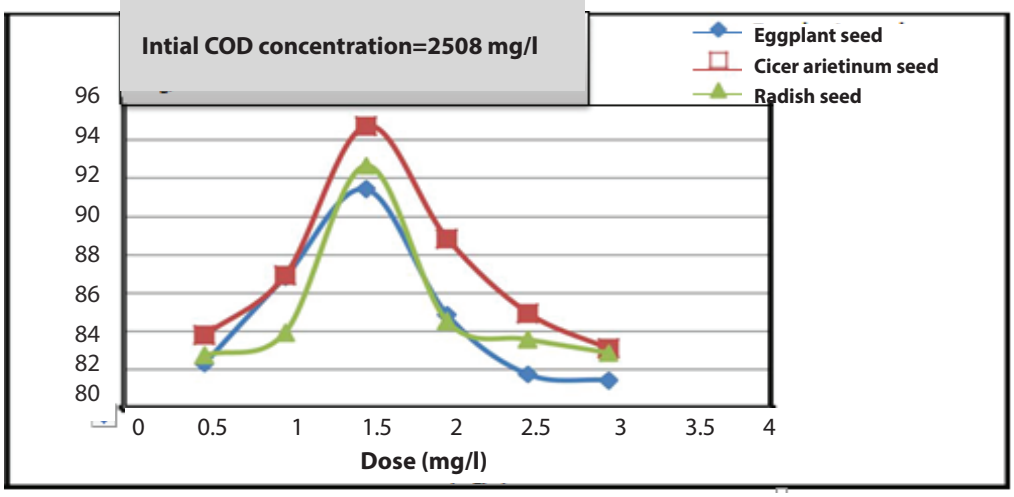

Figure 3: Effect of natural coagulants dose on COD removal.

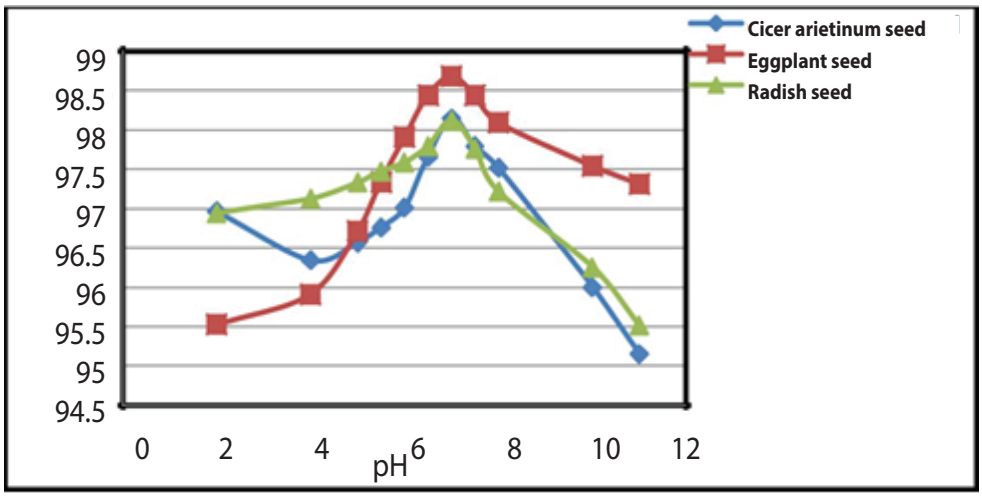

Figure 4: Effect of pH on turbidity removal.

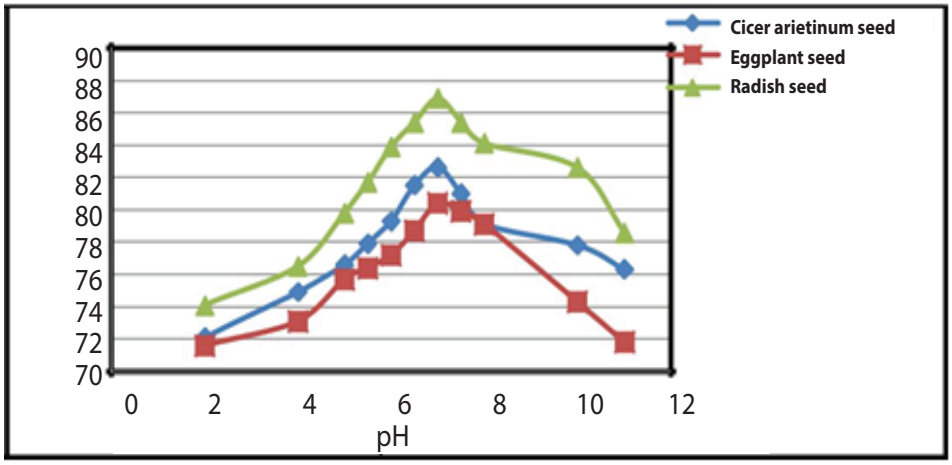

Figure 5: Effect of pH on oil removal.

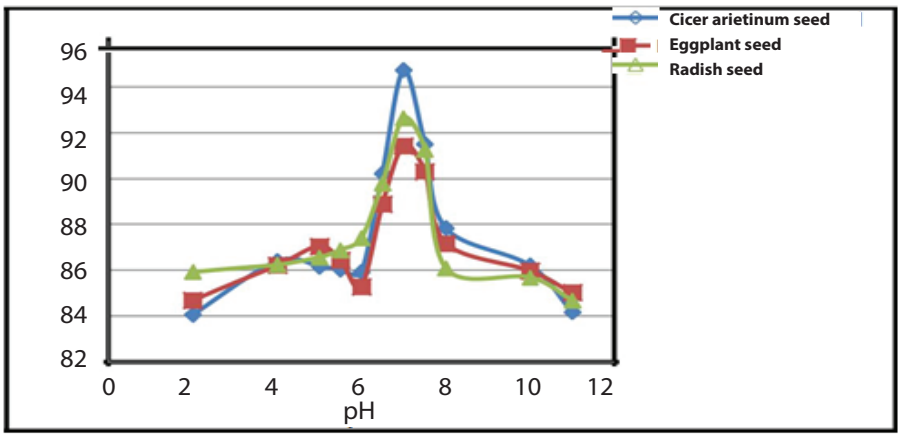

Figure 6: Effect of pH on COD removal.

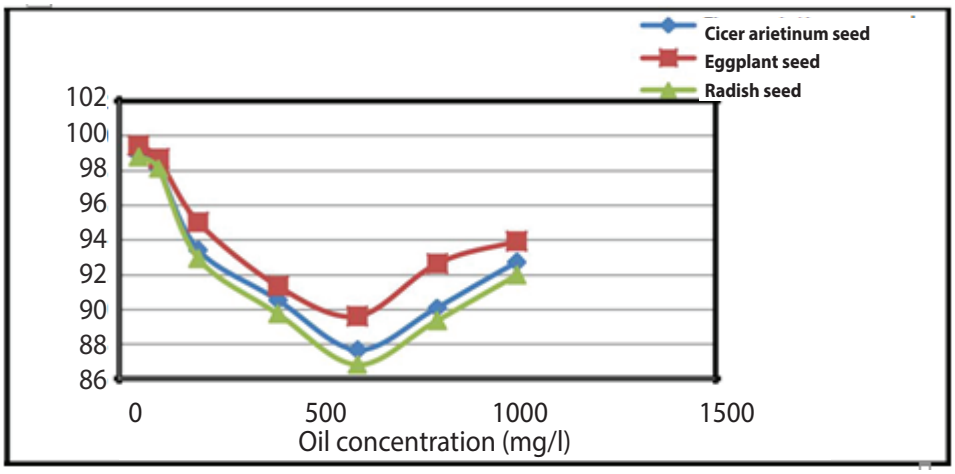

Figure 7: Effect of oil concentration on turbidity removal.

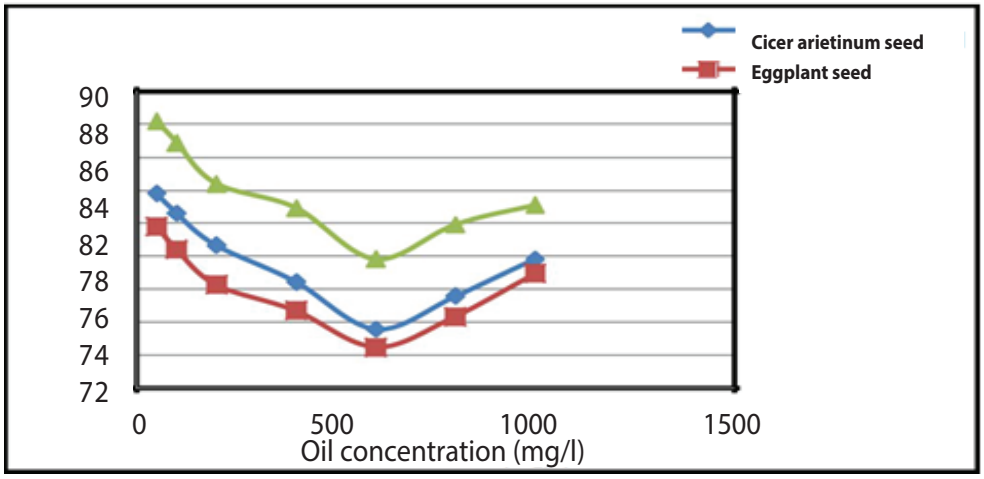

Figure 8: Effect of oil concentration on oil removal.

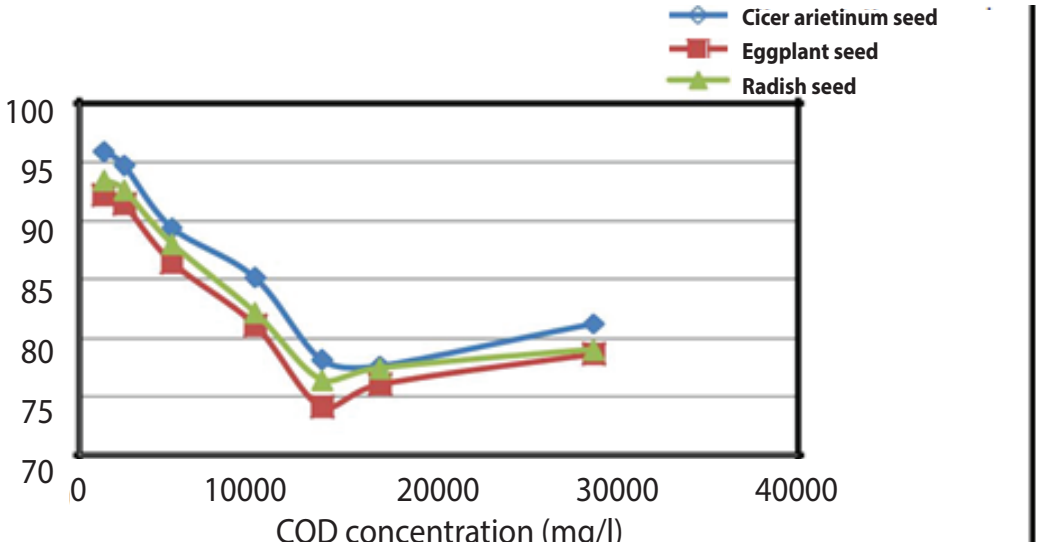

Figure 9: Effect of COD concentration on COD removal.

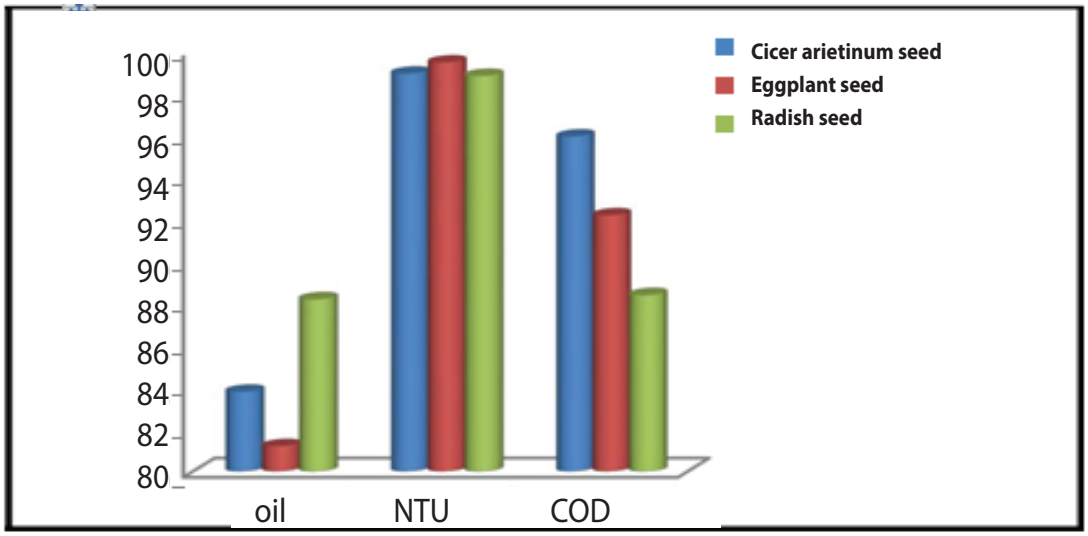

Figure 10: The optimum results obtained from treatment of the produced water sample by using different natural coagulants.

Parameters	Range
COD (mg/L)	1357-28609
TDS (mg/L)	100000
Oil & grease (mg/L)	50-10000
Turbidity (NTU)	435
pH	2-11
Abbreviations: COD: Chemical Oxygen Demand; TDS: Total Dissolved Solids.	

Table 1: Qualitative characteristics of synthetically produced water.

Determination of optimum oil concentration

The results are shown in Figures 7, 8 and 9. Different oil concentrations (50-1000) mg/L and COD (1357 - 26809) mg/L were used. These figures show that the removal efficiency for turbidity, Oil and COD is decreased by increasing the oil concentration from 50 to 600 mg/L and COD concentration from 1357-13514 mg/L. However, an increase in the removal efficiency of pollutants was noted when the concentration of oil and COD was more than 600 mg/L and 13514 mg/L. This increase in the removal efficiency of pollutants caused by the flotation drops of oil to the surface of produced water, resulting in higher oil concentration. It is found from Figure 7 that the higher removal of turbidity R=(99.42%) (2.49 NTU) when add 2 mg/L of the eggplant seed, while the Figure 8 explains the result of removal efficiency of oil, the optimum oil is 50 ppm when using radish seed that gives (R%=88.2), (residual=5.9 mg/L). It can be seen from Figure 9 that the best COD reduction is 65.1 ppm at COD concentration=1357 ppm by using *cicer areitiem* seed as a coagulant at the optimum parameter.

Comparison of natural coagulants at the optimum conditions

The optimum results obtained at the optimum natural coagulants dosage 1.5 mg/L, pH 7, COD concentration 1357 mg/L and oil concentration 50 mg/L by using all types of coagulants for oil removal and COD but 1.5 mg/L by using *Cicer arietinum* seed and 2 mg/L by using eggplant and radish seed for turbidity removal are shown in Figure 10 below. These results manifest that the *Cicer arietinum* seed is the best coagulant for reduction of COD, while radish seed gives the best removal of oil content in produced water and the maximum removal of turbidity was by using eggplant seed but the removal of turbidity when using *Cicer arietinum* seed and radish seed is approximately similar.

Conclusion

In this work, the application of the coagulation/ flocculation process oil field produced water was studied by using different types of natural coagulant, and it was proved to be an efficient and promising method. The natural coagulant of eggplant seed, when used as a coagulant, seems to be more effective than *Cicer arietinum* seed and radish seed for reduction of turbidity while the radish seed is more effecive than eggplant seed and *Cicer arietinum* seed for reduction of oil content from wastewater. *Cicer arietinum* is more efficient in reducing of COD when compared with the other two coagulants that used; this is depending on the presence of protein in the natural coagulant. The highest removal of oil, COD and turbidity were 99.42%, 88.2% and 95.91% with Eggplant plant, Radish and *Cicer arietinum* seed, respectively. The natural coagulant as a coagulant instead of commercial alum can be suggested to be used for the sedimentation process because of its efficiency, availability of sources, low cost and biodegradability, producing less amount of sludge and no change occurs in the value of water pH during the process treatment.

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