Desorption of crude oil from contaminated sand using surfactants*

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Desorption Isotherm,
Kinetics,
Contaminated Sand,
Surfactants.

ABSTRACT

Oil spill is a form of pollution that involves the release of oil into the environment. Oil forms an exterior coating on sand particles and due to its hydrophobicity, it is not washed away easily. It remains in soil matrix for a long time. This oil coating can be removed by different methods which include Shoreline flushing, solvent washing, booms, vacuum desorption, sorbents, biodegradable agents, microbial agents, bio-surfactants, incineration and mechanical removal. Desorption of the oil from the oil-sand-water mixture can be done using surfactants. Our basic aim is to remove crude from the contaminated sand which we came across different methods such as excavation, incineration, thermal desorption, composting, land farming and soil washing. We found that soil washing technique was easier compared to any other techniques based on their availability. The desorption of crude oil was done using anionic surfactant (SDS) and natural surfactant (Reetha). Based on this, different adsorption isotherms were applied and kinetics of desorption were studied.

1. Introduction

Soil washing method is widely used water based method to remove contaminants, in majority of the cases water is mixed with surfactants to aid desorption. Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. A surfactant molecule contains both an oil-soluble component and a water-soluble component is hence called amphiphilic molecule. Surfactant diffuses into water and absorbs at the interface between oil and water it reduces the interfacial tension between oil and water, thus aids in the removal of oil. Surfactants are further classified into Synthetic surfactants and Natural surfactants, Synthetic surfactants are those synthesized using chemicals. Ex: sodium dodecyl sulphate (SDS), Cetrimonium bromide (CTAB) etc. whereas Natural surfactants are available in nature. These are classified into two types Bio-Surfactants synthesized from living organisms such as microbes (Ex: Acinetobacter calcoaceticus) and Plant surfactants derived from plant cells. Ex: Reetha, Sheekakayi. Natural surfactants have comparable properties to chemical surfactants and they also sometimes show better efficiency in high pH and high temperature conditions. These are less toxic to the environment, bio-degradable and renewable.

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In our experiment the surfactants used are sodium dodecyl sulphate (SDS) which is anionic surfactant and Reetha which is a natural surfactant; Reetha: It is a natural plant surfactant known as soap nut. These are generally Oligo glycosides. They are very popular and are grown in south Asia. They can be used as an alternative to SDS, due to their similar cleansing property as detergent. They are bio-degradable, non-toxic and renewable. Batch wise desorption process is done using these surfactants. Based on the efficiencies of these surfactants; different adsorption/desorption isotherms [32] were applied such as Langmuir isotherm, Freundlich isotherm, and The Dubinin-Radushkevich isotherm [42] and desorption kinetics [39] such as Pseudo-Second Order Rate, Elovich and Intra-particle diffusion models were applied and are compared with the experimental data's. Desorption of oil (i.e. percentage removal of crude oil from contaminated sand) was determined based on type of surfactants used, concentrations of surfactants and based on RPM.

2. Materials and Methods

The sand was sieved using 22 and 25 BSS mesh screens and the oversize fraction of 25 and undersize of 22 BSS screen was collected. Sand were thoroughly washed and treated with different chemicals so as to remove dirt and impurities. And was dried at 50-60^oC for 12 hours and kept in closed air tight container to avoid action of moisture. The treated sand was contaminated with crude oil (brass river crude oil) proportionally and weathering was done. The surfactant solution was prepared by mixing specified amount of measured surfactant in the distilled water for specified time in a magnetic stirrer at 1200 RPM. In case of plant surfactant the solution is filtered using a 53 micron mesh and centrifuged.

Procedure for Desorption kinetic study: A measured amount of contaminated sand is taken in a conical flask and it is treated with the surfactant solution at a specified RPM. The test samples are taken out at different interval of time. (Between 0 to 96h). In case of concentration study the samples are taken out at equilibrium time. The liquid is decanted at each time interval from the conical flask. In case of surfactant solution 10ml of distilled water is added after decanting the liquid and it is shaken for 10 minutes in the shaker. This step is repeated twice; to dilute the concentration of surfactant. The distilled water added to the sample is decanted and dried in oven at 40^oC for 1h. Extraction was done and the samples were analyzed under U-Vis spectrometer with wavelength of 395nm.

Spectrometer study: Calibration chart for Crude in hexane

Calibration chart for the concentration of crude oil in hexane solution was obtained using a Jasco UV spectrometer at a wavelength of 395nm.

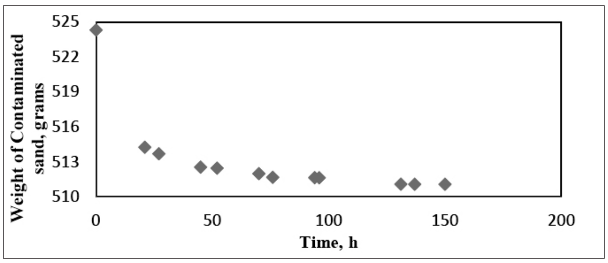

Fig. 1.1. Sand weathering.

The concentration of crude oil on sand before and after washing was determined. The absorbance for various concentrations of Crude oil was calculated using Calibration chart.

3. Results and Discussion

1. Sand weathering

The results of Sand Weathering were plotted with weight of the contaminated sand in (grams) vs time in (hours). It was observed that the weight of sand reduced drastically in the first 24 hours and then gradually stabilized at 130 hours. From the obtained data, the time for weathering was determined to be 130 hours. (Ref. Fig. 1.1)

2. Calibration chart

The absorbance for the various concentrations of crude oil in hexane solutions are plotted with Absorbance vs Concentration in weight percentage (Wt. %).

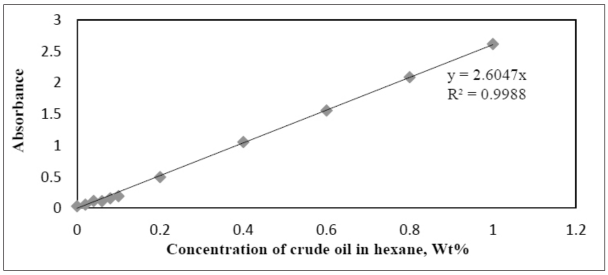

Fig. 2.1. Calibration chart for U-Vis spectrometer.

3. Kinetic studies

3.1. Desorption kinetics study using distilled water

Experimental data has been plotted with concentration of crude oil on sand in (gram of crude oil/gram of sand) vs time in (hours).

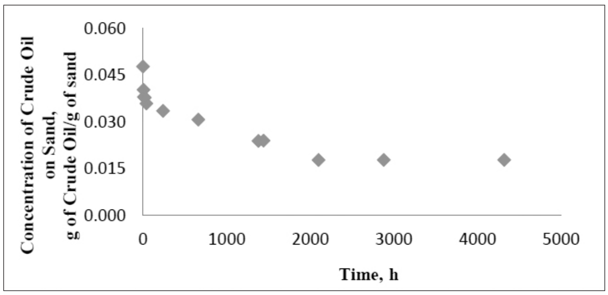

Fig. 3.1. Desorption kinetic study using distilled water.

The concentration of crude oil on sand decreased till 24 hours and thereafter remained constant. Thus the equilibrium time for desorption was determined to be 24 hours.

Pseudo-Second-Order rate model:

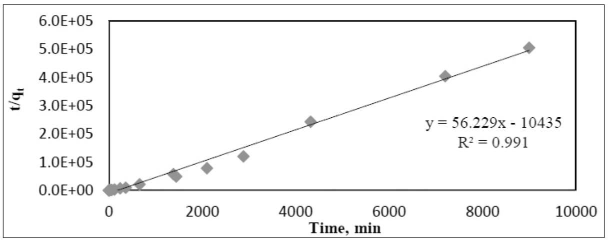

Fig. 3.1.1. Pseudo second order rate model for distilled water.

Elovich model:

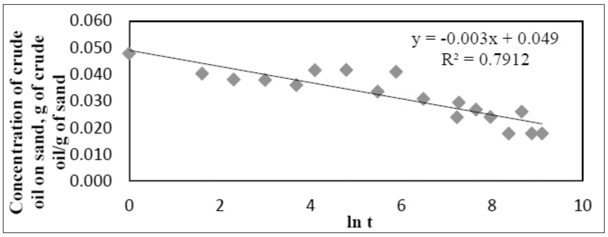

Fig. 3.1.2. Elovich Model for desorption using Distilled water.

Intra-Particle Diffusion Model:

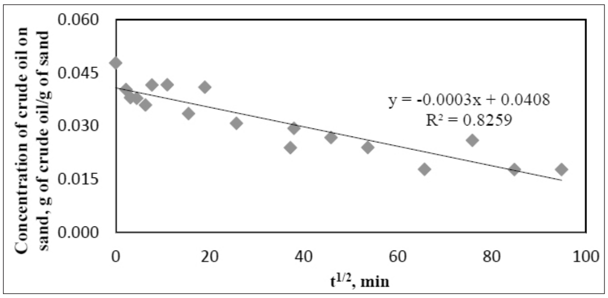

Fig. 3.1.3. Intra-Particle Diffusion Model using Distilled water.

High R^2 value is derived by fitting the experimental data into Pseudo-Second-Order rate model (R^2>0.991), as compared with the Elovich model (R^2>0.791) and Intra-Particle Diffusion Model (R^2>0.825).

This suggests that Pseudo-Second-Order rate model can generate a satisfactory fit to the experimental data, while Elovich and Intra-Particle Diffusion Model cannot.

3.2. Desorption kinetics study using sodium dodecyl sulphate (SDS)

Experimental data has been plotted with concentration of crude oil on sand in (gram of crude oil/gram of sand) vs time in (hours).

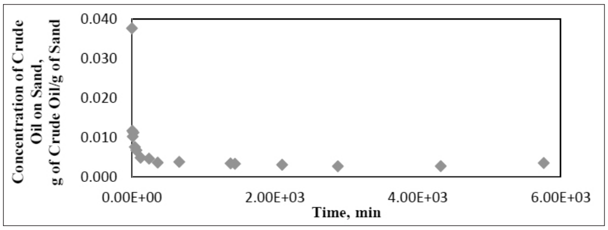

Fig. 3.2. Desorption kinetic study using (SDS).

The concentration of crude oil on sand decreased till 6 hours and thereafter remained constant. Thus the equilibrium time for desorption was determined to be 6 hours.

Pseudo-Second-Order rate model:

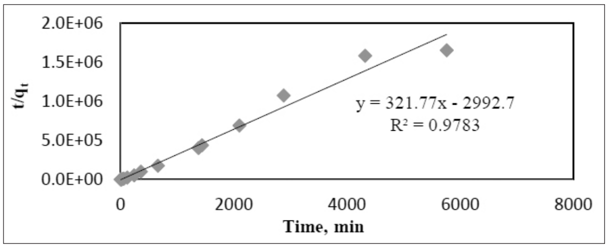

Fig. 3.2.1. Pseudo-second-order rate model using SDS.

Elovich model:

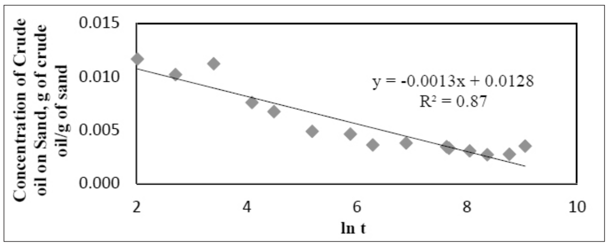

Fig. 3.2.2. Elovich model for desorption using SDS.

Intra-Particle Diffusion Model:

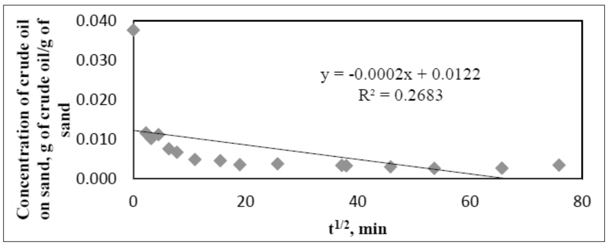

Fig. 3.2.3. Intra-particle diffusion model using SDS.

High R^2 value is derived by fitting the experimental data into Pseudo-Second-Order rate model (R^2>0.978), are compared with the Elovich model (R^2>0.870) and Intra-Particle Diffusion Model (R^2>0.268).

This suggests that Pseudo-Second-Order rate model can generate a satisfactory fit to the experimental data, while Elovich and Intra-Particle Diffusion Model cannot.

3.3. Desorption kinetics study using REETHA

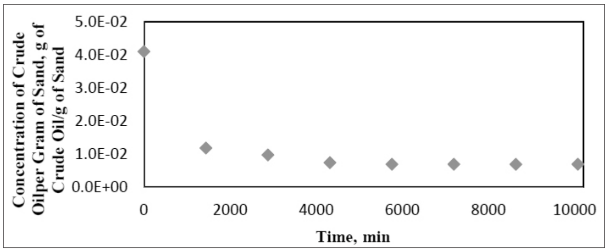

Fig. 3.3. Desorption kinetic study using reetha.

The concentration of crude oil on sand decreased till 96 hours and thereafter remained constant. Thus the equilibrium time for desorption was determined to be 96 hours.

Pseudo-Second-Order rate model:

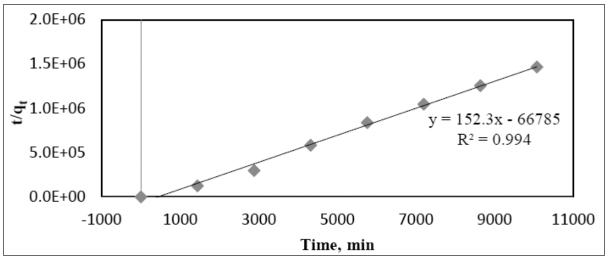

Fig. 3.3.1. Pseudo-second-order rate model for desorption using Reetha.

Elovich model:

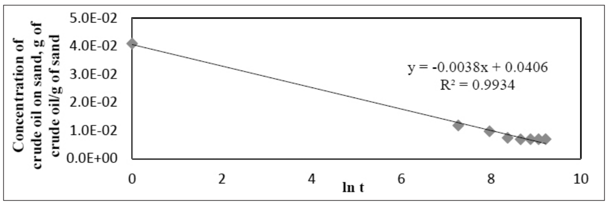

Fig. 3.3.2. Elovich model for desorption using Reetha.

Intra-Particle Diffusion Model:

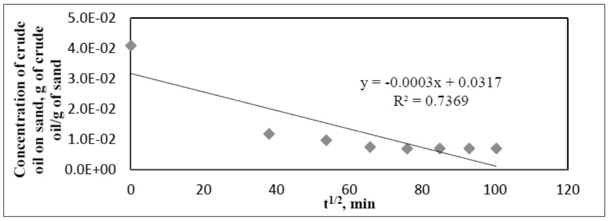

Fig. 3.3.3. Intra-particle diffusion model for desorption using Reetha.

High R^2 value is derived by fitting the experimental data into Pseudo-Second-Order rate model (R^2>0.994) and Elovich model (R^2>0.993), are compared with Intra-Particle Diffusion Model (R^2>0.736).

This suggests that Pseudo-Second-Order rate model and Elovich model can generate a satisfactory fit to Experimental data, while Intra-Particle Diffusion model cannot.

4. Effect of type of surfactants, concentrations and RPM

4.1. Desorption of crude oil using different concentrations of SDS

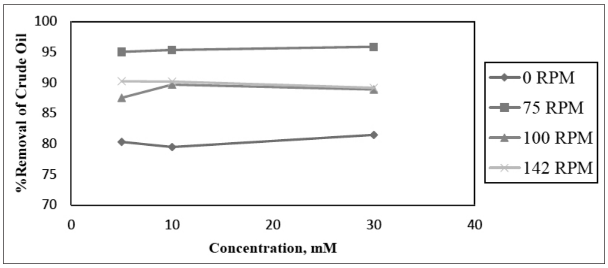

Fig. 4.1.1. Effect of RPM on % removal of crude oil.

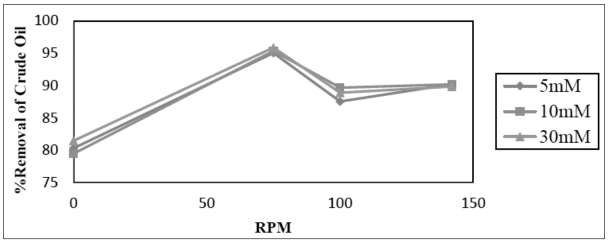

Fig. 4.1.2. Effect of concentration on % removal of crude oil.

It was observed that the removal was the highest (i.e. 95%) for 75 RPM. And for a particular RPM, with increase in surfactant concentration, the increase in removal was marginal.

4.2. Desorption of crude oil using different concentration of REETHA:

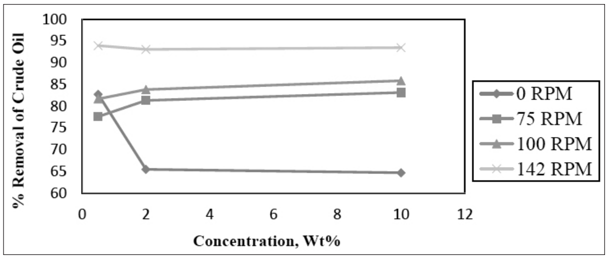

Fig. 4.2.1. Effect of RPM on % removal of crude oil.

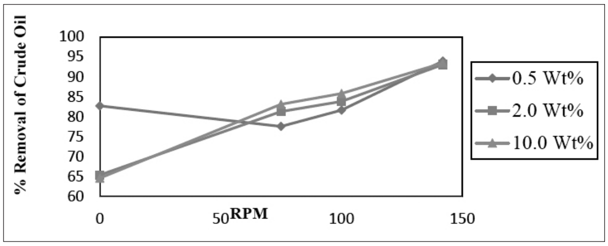

Fig. 4.2.2. Effect of concentration on % removal of crude oil.

It was observed that the optimum speed for Reetha is 142rpm and the removal efficiency 93%.

4.3. Desorption of crude oil using distilled water

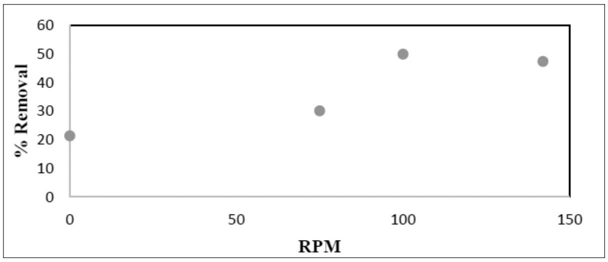

Fig. 4.3. Effect of RPM on % Removal of Crude oil.

It was observed that the optimum speed for Distilled Water is 100 RPM and the removal efficiency 49.88%.

5. Desorption Isotherms

5.1. Desorption isotherm for removal of crude oil using SDS

An equilibrium graph has plotted based on the amount of oil present on the sand with respect to the amount of oil in surfactant solution for both sodium dodecyl sulphate (SDS) and Reetha solutions.

Langmuir Isotherm: Figure 5.1.1 display the fitting of experimental data to the linearized form of Langmuir isotherm.

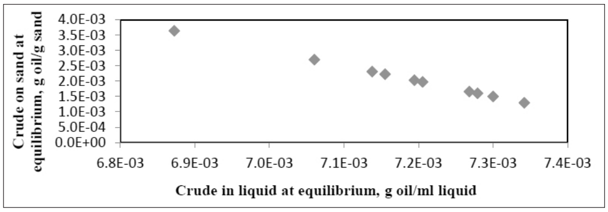

Fig. 5.1. Desorption of crude oil using SDS.

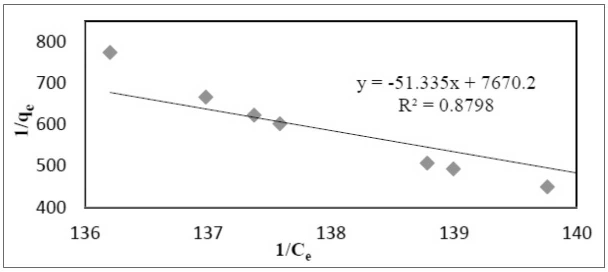

Fig. 5.1.1. Langmuir isotherm for desorption using SDS.

Freundlich Isotherm: Figure 5.1.2 display the fitting of experimental data to the linearized form of Freundlich isotherm.

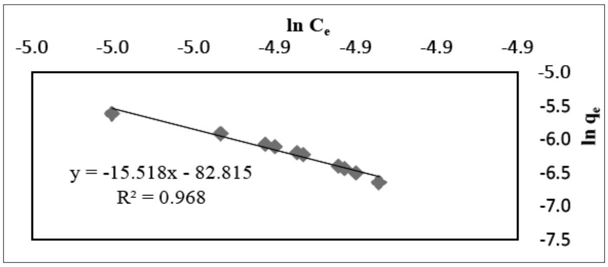

Fig. 5.1.2. Freundlich isotherm for desorption using SDS.

Dubinin-Radushkevich Isotherm: Figure 5.1.3 display the fitting of experimental data to the linearized form of Dubinin-Radushkevich isotherm.

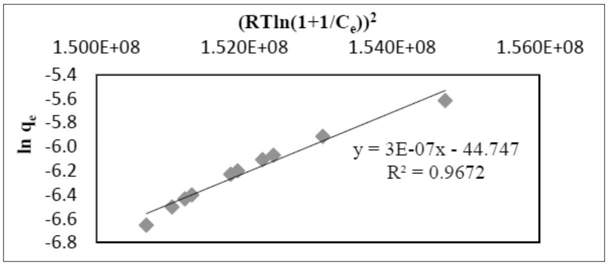

Fig. 5.1.3. Dubinin-radushkevich isotherm for desorption using SDS.

High R^2 value is derived by fitting the experimental data into Freundlich model (R^2>0.968), D-R model (R^2>0.967) as compared with the Langmuir model (R^2>0.878).

This suggests that Freundlich and D-R isotherm models can generate a satisfactory fit to the Experimental data, while Langmuir isotherm cannot.

5.2. Desorption isotherm for removal of crude oil using Reetha

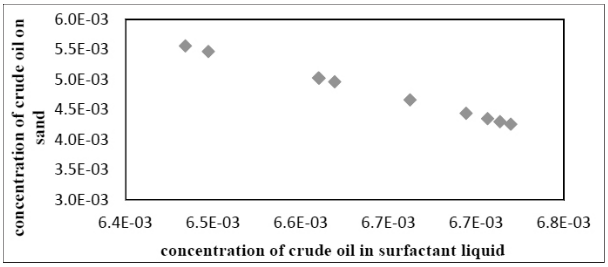

Fig. 5.2. Desorption of crude oil at equilibrium.

Langmuir Isotherm: Figure 5.2.1 display the fitting of experimental data to the linearized form of Langmuir isotherm.

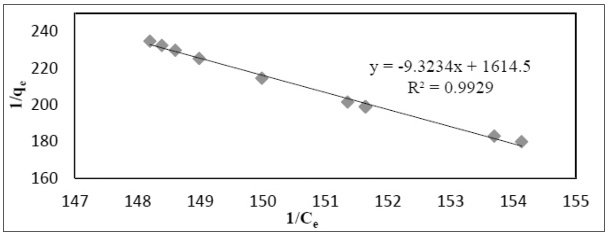

Fig. 5.2.1. Langmuir isotherm for desorption using Reetha.

Freundlich Isotherm: Figure 5.2.2 display the fitting of experimental data to the linearized form of Freundlich isotherm.

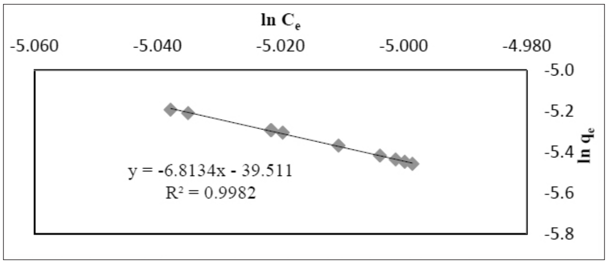

Fig. 5.2.2. Freundlich isotherm for desorption using Reetha.

Dubinin-Radushkevich Isotherm: Figure 5.2.3 display the fitting of experimental data to the linearized form of Dubinin-Radushkevich Isotherm.

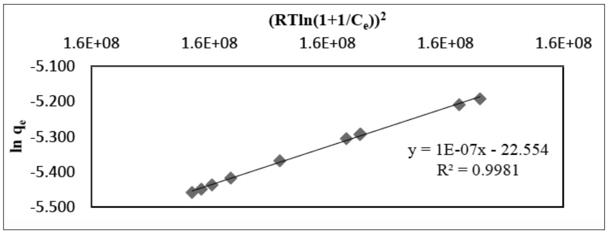

Fig. 5.2.3. Dubinin-Radushkevich isotherm for desorption using Reetha.

High R^2 value is derived by fitting the experimental data into Freundlich model (R^2>0.996), D-R model (R^2>0.998) and with the Langmuir model (R^2>0.998).This suggests that all three isotherms gives the satisfactory fit to the Experimental data.

Conclusion

The weathering time for the crude oil contaminated sand was determined to be 5.5 days. Desorption kinetic studies of all the surfactants followed the Pseudo Second Order Model (PSMO). The equilibrium washing times for Distilled Water, Sodium dodecyl sulphate (SDS) and Reetha were determined to be 24 hours, 6 hours and 96 hours respectively. RPM is an important parameter for the removal using SDS and Reetha and the variation of concentration at a particular RPM improved the removal only marginally. It was observed that the optimum speed for SDS and Reetha was 75 rpm and 142 rpm and the maximum % removal for SDS and Reetha was 90% and 93%. The natural surfactant Reetha could give a better removal than SDS. The desorption isotherm data indicated that the adsorption of crude on sand is physical adsorption. However, further work needs to be done at different temperature to determine the activation energy/Heat of desorption.

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