



Adsorption Chemistry of Oil-in-Water Emulsion from Spent Oil Based Cutting Fluids Using Sawdust of *Mangifera indica*

Sandeep Tiwari^{1,*}, Vimal K. Gupta², P.C. Pandey³, H. Singh⁴, P.K. Mishra⁵

¹Mechanical Engineering Department, GLA Institute of Technology & Management, Mathura, India, ²Mechanical Engineering Department, GLAITM, Mathura, India, ³Mechanical Engineering Department, IIT, Roorkee India, ⁴Mechanical Engineering Department, KNIT, Sultanpur India, ⁵Mechanical Engineering Department, IT BHU, Varanasi, India

Received July 24, 2008; Accepted November 19, 2008

Abstract: Freundlich and Langmuir theories of surface chemistry for the adsorption of emulsified oil from spent cutting fluid generated by the use of semi-synthetic metal working fluid in metal machining operations using sawdust of *Mangifera indica* through batch adsorption study under optimized adsorptive pertinent factors were studied in the present research work. Adsorption of emulsified oil was favoured at low pH with maximum removal at pH=3 and temperature of 25 °C. Mathematical adsorption isotherms were predicted using linearized plots of adsorbed oil per unit weight of sawdust versus equilibrium oil-in-water concentration. These predicted isotherm model were compared with the Freundlich and Langmuir models. Numerical analysis has been used to calculate correlation coefficient of experimental observed adsorbed oil with predicted models. Results of present study for Freundlich and Langmuir kinetics for adsorption show the applicability of these theories for the adsorption of emulsified oil from semi-synthetic metal working fluid.

Key words: Adsorption, Freundlich Isotherms, Langmuir Isotherms, Semi-synthetic Metal Working Fluid

Symbols

- C_0 Initial oil concentration, $mg\ L^{-1}$
 C_e Adsorbate equilibrium oil concentration, $mg\ L^{-1}$
 C_t Oil concentration at time of t, $mg\ L^{-1}$
 k Freundlich Constant (i.e. Adsorption Capacity)
 k_1 Langmuir Empirical Constant (i.e. Equilibrium constant), $L\ (mg)^{-1}$
 k_2 Langmuir Empirical Constant (i.e. Adsorption Capacity), $mg\ (gm)^{-1}$
 m_s Weight of adsorbent, gm .
 n Freundlich Constant (i.e. Adsorption Intensity)
 Q_e Oil removed per unit weight of adsorbent, $mg\ (gm)^{-1}$
 Q_t Adsorbed oil per unit weight of adsorbent at time t, $mg\ (gm)^{-1}$
 V volume of the SCF, L

Introduction

Metal Working Fluids (MWF) have found extensive applications in metal working industries to improve the friction conditions between the tool and work and carry away the heat generated due to metal machining (McCoy, 1994). This has also been found to improve the tool life, work surface finish and metal removal rate. In addition, they help to carry the swarf away from the working area and protect the newly formed surface. MWF are complex mixture that may contain petroleum products, vegetable and animal fats, organic/inorganic salts and wide variety of additives. MWF can be grouped into four major categories: straight MWF, which are undiluted mineral and fatty oils; soluble MWF, which are water emulsions of mineral and fatty oils; synthetic MWF, which are chemical solutions of organic compounds and inorganic salts in water; and semi-synthetic MWF, which are emulsions of mineral oils with water and the chemicals found in synthetics (NIOSH, 1998).

Once MWF has been used for a period, its degradation with time is unavoidable and it generates toxic liquid waste known as Spent Cutting Fluid (SCF). Due to increasing concern for environmental protection, it has now become mandatory to process the SCF before they can be disposed off into the environment safely.

*Corresponding: E mail: sandeep_tiwari1970@rediffmail.com, Tel: +91-5662-250900, Fax: +91-5662-241687

Till date, wide range of approaches through researches for the removal of emulsified oil from SCF generated by the use of semi-synthetic MWF are in existence and frequently used in industrial wastewater treatment plants. These include physical and chemical precipitation through settlings, centrifugation, pasteurization, skimmers, ultra-filtration, coalescence, straining, deep bed filtration, ion exchange, reverse osmosis, nano-filtration, coaxial micro-filtration *etc* (Benito & Ruiz, 2002; Mathavan & Viraraghavan 1992; Rengaraj *et al.*, 2001; Solisio *et al.*, 2002; Viraraghavanet & Mathavan, 1990; Yurlova *et al.*, 2002). Adsorption phenomenon is being used worldwide by the environmental engineers to separate many organic/inorganic compounds from industrial wastewater. But, in case of SCF, it is rarely used in any industrial treatment plants to separate emulsified oil.

In the present study, innovative work has been done for the study of adsorption kinetics of emulsified oil from SCF. For this purpose, batch adsorption study was conducted using sawdust of *Mangifera indica* in the form of USMI and TSMI as the adsorbent. Applicability of Freundlich and Langmuir theories for oil adsorption has been analyzed using the experimental results of batch adsorption study.

Material and Methods

Adsorbent Preparation

Sawdust of *Mangifera indica* (*i.e.* Mango tree) found in the country region of India was used as an adsorbent for the study of adsorption kinetics of emulsified oil from SCF. Collected sawdust from timber working shop situated near agriculture land areas was washed to clean the adhering dirt, rinsed thoroughly with double distilled water and finally heated in oven at 105 °C for 24 hrs. After drying, it was ground to a fine powder and to make homogenous it was sieved through 177 µm and retained part of sawdust on 100 µm sieve was used as adsorbent and named as Unmodified Sawdust of *Mangifera Indica* (USMI).

Activation of Adsorbent

To remove any debris or soluble bio-molecules which may be interacted with metal ion during sorption, dried form of sawdust retained on 100 µm sieve was further treated with highly concentrated H₂SO₄ in the ratio of 1:1 (w/v ratio *i.e.* one mg of sawdust with one ml of acid) in a muffle furnace for 24 hrs at 150 °C. The heated material was washed with double distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The material was dried in an oven at 105 °C for 24 hrs. After that it was grounded and homogenized by passing it with sieve of 177 µm and retained part on 100µm sieve was used as chemically modified activated carbon and named as Treated Sawdust of *Mangifera indica* (TSMI). All adsorbents were dried at 105 °C overnight before any adsorption experiments.

Adsorbate Solution

The metalworking fluid used in this work is Hysol G, SDS # 7040, a semi-synthetic oil prepared by Castrol Limited which gives a micro-emulsion when mixed with water. Liquid waste in the form of emulsified oil generated after the use of Hysol G in metal working operations as spent cutting fluid was collected from M/s Timken India Limited, Tata Nagar, India. Adsorbate solution samples were prepared in the proportion of 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5% and 6.0% (v/v ratio) of emulsified oil for the batch adsorption study.

Analysis of Oil-in-water Emulsion

The concentrations of oil in the aqueous solution were measured by hand refractometer. In refractometer, principle of refraction of light is used and by means of external light interference refractive index of sample is measured which gives the concentration of oil. It is based on the phenomena that as density of a substance (*i.e.* concentration) increases its refractive index rises in proportionate manner (Hilal *et al.*, 2004).

Batch Adsorption Studies

Batch adsorption experiments to study the adsorption kinetics of emulsified oil through adsorbent of USMI and TSMI were conducted. Concentration of adsorbate solution samples were

taken in the proportion of 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 5.5% and 6.0%. Experiments were carried out by adding 25 gm of adsorbent in one litter of each proportion of SCF. Quantity of 50 ml from each proportion was taken for the batch adsorption study. Adjustment of pH was carried out using 0.1 N NaOH and/or 0.1 N H₂SO₄. Agitation of the system under investigations was carried out on orbital thermal shaker.

To maximize emulsified oil removal by the adsorbents, batch experiments were conducted at ambient temperature (*i.e.* 25°C) using the optimum conditions of all pertinent factors such as adsorbent dose, pH, agitation speed, contact time (Chakravarty *et al.*, 2002). Subsequent adsorption experiments were carried out with only optimized parameters. Adsorption isotherms were carried out in the reaction mixture consisting of 25 gm (L)⁻¹ of adsorbent and 50 ml of emulsified oil of SCF solution with varying initial oil concentration from 12.3 mg (L)⁻¹ to 49.2 mg (L)⁻¹. The change in oil concentration due to adsorption was determined using hand refractometer. The amount of emulsified oil adsorbed per unit weight of adsorbent was computed by the following mass balance equation;

$$Q_t = \frac{(C_o - C_t)V}{m_s} \quad (1)$$

Where Q_t is the weight of oil removed from SCF per unit weight of adsorbent in mg(gm)⁻¹, C_o and C_t are the concentration of oil initially and at given time t , respectively in mg(L)⁻¹, V is the volume of the SCF in *litter* and m_s is the weight of adsorbent (*i.e.* sawdust) in *gm*. Percentage removal of oil (R %) in solution was calculated using following equation;

$$R (\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in duplicate and the mean values of two data sets are presented. When the relative error exceeded the relative standard deviation by more than 1.0%, the data were disregarded and a third experiment was conducted until the relative error fell within the acceptable range.

Numerical Analysis

Adsorption kinetics of emulsified oil has been assessed by minimizing the sum of square of errors between the experimental observed data and the predicted isotherm models with the application of linear least square regression method (Bethea, *et al.*, 1985).

Result and Discussion

Adsorption Equilibrium Isotherms

The physical chemistry involved for adsorption is complex phenomena and no single theory of adsorption till date has been put forward to explain all the adsorptive principles of adsorption systems. Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption and desorption, while others are intended to correlate the experimental data in simple equations with several empirical parameters (Chakraborty *et al.*, 2005). In the present study, Freundlich and Langmuir theory of surface chemistry for adsorption at solid-liquid interface has been used to study of adsorption kinetics of emulsified oil.

Results of batch adsorption for adsorbed oil per unit weight of adsorbents versus equilibrium solute concentration have been plotted in Fig 1. Numerical analyses have been used to predict mathematical Freundlich and Langmuir Models. Predicted mathematical models have also been plotted in Figure 1.

Freundlich Isotherm Model

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. Heterogeneity of the surface and the exponential distribution of adsorbent and their energies can be defined by the by Freundlich isotherm (Freundlich, 1906). Eq. 3 represent Freundlich adsorption

isotherm to explain the variation of adsorption with concentration over a limited range at constant temperature.

$$Q_e = k_f C_e^{1/n} \quad (3)$$

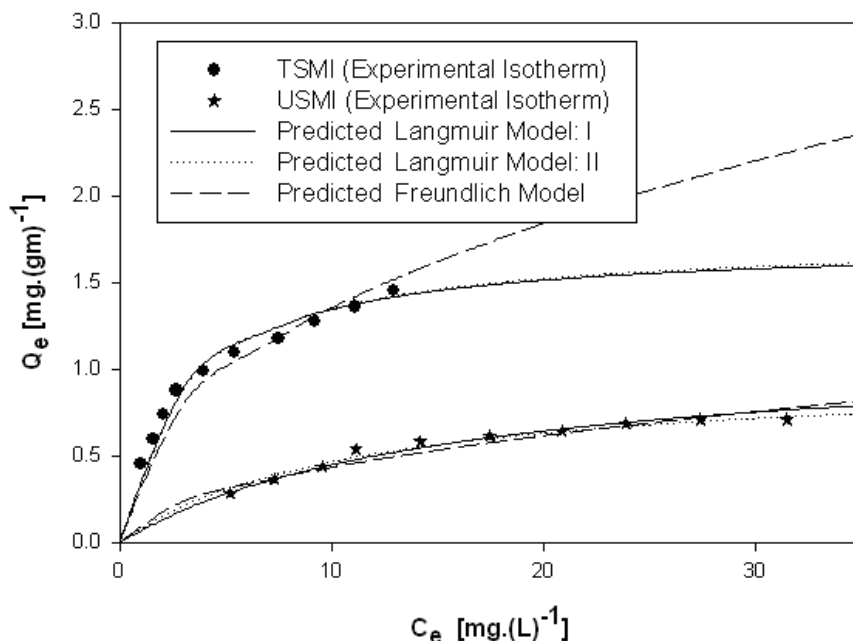


Figure 1: Experimentally observed isotherms and predicted isotherms by Freundlich and Langmuir Model I & II for both adsorbents. Isotherms are plotted between adsorbed emulsified oil per unit weight of adsorbent in $mg\ gm^{-1}$ versus equilibrium concentration of solute in $mg\ L^{-1}$. Experimental Parameters, Initial Oil Concentration: from $12.3\ mg\ L^{-1}$ to $49.2\ mg\ L^{-1}$, Adsorbent dose: $25\ gm\ L^{-1}$, $pH = 3$, Temperature: $25\ ^\circ C$, Agitation speed: $150\ rpm$ and Particle Size: $177-100\ \mu m$.

Where Q_e is the oil removed per unit weight of adsorbent in $mg\ (gm)^{-1}$, C_e is the adsorbate equilibrium oil concentration in $mg\ (L)^{-1}$, k_f and n are Freundlich constants. On linearization, Eq. 3 can be written by Eq. 4 and known as linearised Freundlich isotherm model.

$$\ln(Q_e) = \ln(k_f) + \frac{1}{n} \ln(C_e) \quad (4)$$

Logarithmic plot of Q_e and C_e obtained from batch study has been plotted in Figure 2. Batch adsorption experimental data were observed at the optimized conditions of all pertinent factors such as pH, adsorbent particle size, dose, temperature and agitation speed at initial oil concentration from $12.3\ mg\ L^{-1}$ to $49.2\ mg\ L^{-1}$. Figure 2 gives straight line having correlation coefficient of 0.966 and 0.981 for adsorbents of USMI and TSMI, respectively, indicating the applicability of Freundlich theory for the adsorption kinetics of emulsified oil from SCF.

Adsorption kinetics has been analyzed with the help of numerical analysis of observed experimental data. Adsorption intensity and adsorption capacity has been determined for both adsorbents and are reported in Table 1. Mathematically, predicted Freundlich isotherm equations for both adsorbent can be written by Equation 5 & 6.

$$\text{For USMI; } Q_e = 0.136C_e^{1/1.983} \quad (5)$$

$$\text{For TSMI; } Q_e = 0.49C_e^{1/2.263} \quad (6)$$

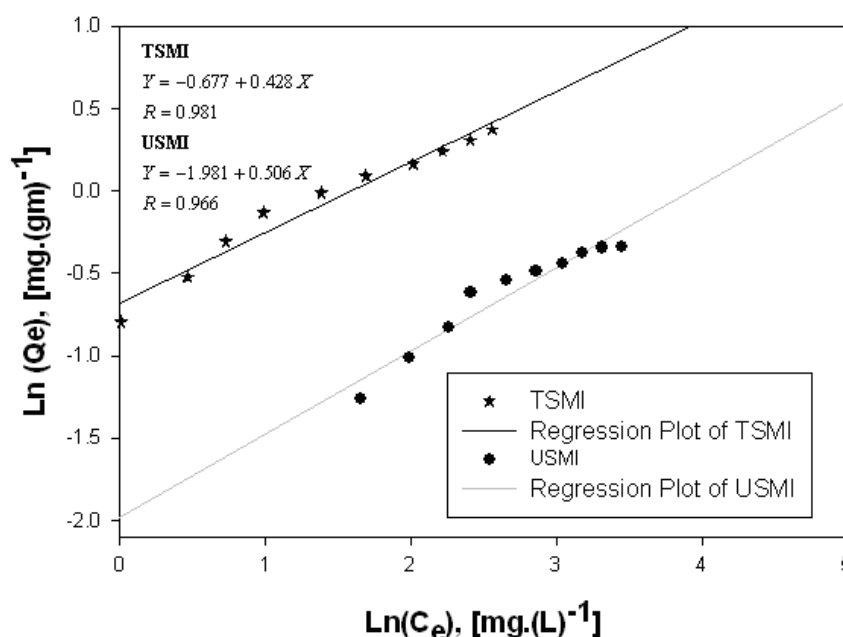


Figure 2: Linearised Freundlich isotherms of USMI & TSMI. Isotherms are plotted in adsorbed emulsified oil from SCF per unit weight of adsorbent in $mg.gm^{-1}$ and equilibrium concentration of solute in $mg.L^{-1}$. Experimental Parameters, Initial Oil Concentration: from $12.3 mg.L^{-1}$ to $49.2 mg.L^{-1}$, Adsorbent dose: $25 gm.L^{-1}$, $pH = 3$, Temperature: $25^{\circ}C$, Agitation speed: 150 rpm and Particle Size: 177-100 μm .

Table 1: Adsorptive parametric constants for Freundlich Model

Adsorptive Parameter	Freundlich	
	USMI	TSMI
Adsorption Intensity, n^a	1.983	2.263
Adsorption Capacity, k_f^b	0.136	0.490
Correlation Coefficients	0.957	0.980

^a It is Freundlich constant known as adsorption capacity, which is dimensionless constant.

^b It is Freundlich constant known as adsorption intensity. It gives an indication of the favourability of adsorption. Value of constant, n : 2-10, represent good; 1-2, represent favorable; and $n < 1$ shows poor adsorption characteristics (Raji & Anirudhan, 1997, Rao & Bhole, 2001). It is dependent upon the adsorption capacity of adsorbent. It is represented by $mg^{1-(1/n)} L^{1/n} gm^{-1}$.

Langmuir Isotherm Model

Irving Langmuir pointed the inherent assumption of surface chemistry for adsorption theory. According to this assumption, rapid falling of intermolecular forces with distance is due to single molecule adsorbed thickness of layer, which is mainly because of availability of fixed localized surface sites present on the homogenous surface of adsorbent molecule (Langmuir, 1918). This view is widely accepted for adsorption at low pressure or at moderately high temperature. On the basis of above principle, Langmuir has developed following equation, known as Langmuir isotherm.

$$Q_e = \frac{k_1 k_2 C_e}{1 + k_1 C_e} \quad (7)$$

Where Q_e is the amount of oil adsorbed per unit weight of adsorbent to form a complete monolayer on the surface in $mg (gm)^{-1}$, C_e is the oil concentration at equilibrium in $mg (L)^{-1}$, k_1 and k_2 are Langmuir empirical constants.

Langmuir Isotherm Model: I

According to linearization by Stumm & Morgan, 1981, Eq.7 can be represented by Eq. 8 and it is known as linearised Langmuir Isotherm Model I.

$$\frac{1}{Q_e} = \frac{1}{k_2} + \frac{1}{k_1 k_2} \left(\frac{1}{C_e} \right) \quad (8)$$

Langmuir Isotherm Model: II

Similarly, linearization according to Weber (1972), Eq. 7 can be represented by Eq. 9 and it is known as linearised Langmuir Isotherm Model II.

$$\frac{C_e}{Q_e} = \frac{1}{k_1 k_2} + \frac{1}{k_2} (C_e) \quad (9)$$

Results obtained from batch study at optimized pertinent adsorptive factors and initial concentration from 12.3 mg (L)^{-1} to 49.2 mg (L)^{-1} are plotted in C_e/Q_e versus C_e and $1/Q_e$ versus $1/C_e$ as shown in Fig 3. Both plots shown in the Fig 3 give straight lines indicating applicability of Langmuir theory for oil adsorption. Numerical analysis has been used for linearised isotherm of Langmuir Model I & II and mathematical isotherms as shown in equation from 10 to 13 are predicted. Adsorption Langmuir constants in terms of equilibrium constant and adsorption capacity are determined and are reported in Table 2.

Table 2: Adsorptive parametric constants for Langmuir Model I & II

Adsorptive Parameter	Langmuir Models			
	Model: I		Model: II	
	USMI	TSMI	USMI	TSMI
Equilibrium constant, $k_1 \text{ [L (mg)}^{-1}]$	0.065	0.353	0.091	0.338
	65 ^d	353 ^d	91 ^d	338 ^d
Adsorption Capacity, $k_2 \text{ [mg (gm)}^{-1}]$	1.145	1.729	0.974	1.748

^c It is Langmuir empirical constant, which is based on the type of analysis. In case of thermodynamic equilibrium, it is affinity parameters, similarly for mass transfer balance, it is affinity parameter. It is temperature dependent and related to the Gibbs free energy and hence it shows the change in enthalpy.

^d If initial concentration of solute is taken in mg.ml^{-1} .

For Langmuir Model I

$$\text{For USMI; } Q_e = \frac{0.074 C_e}{1 + 0.065 C_e} \quad (10)$$

$$\text{For TSMI; } Q_e = \frac{0.61 C_e}{1 + 0.353 C_e} \quad (11)$$

For Langmuir Model II

$$\text{For USMI; } Q_e = \frac{0.089 C_e}{1 + 0.091 C_e} \quad (12)$$

$$\text{For TSMI; } Q_e = \frac{0.591 C_e}{1 + 0.338 C_e} \quad (13)$$

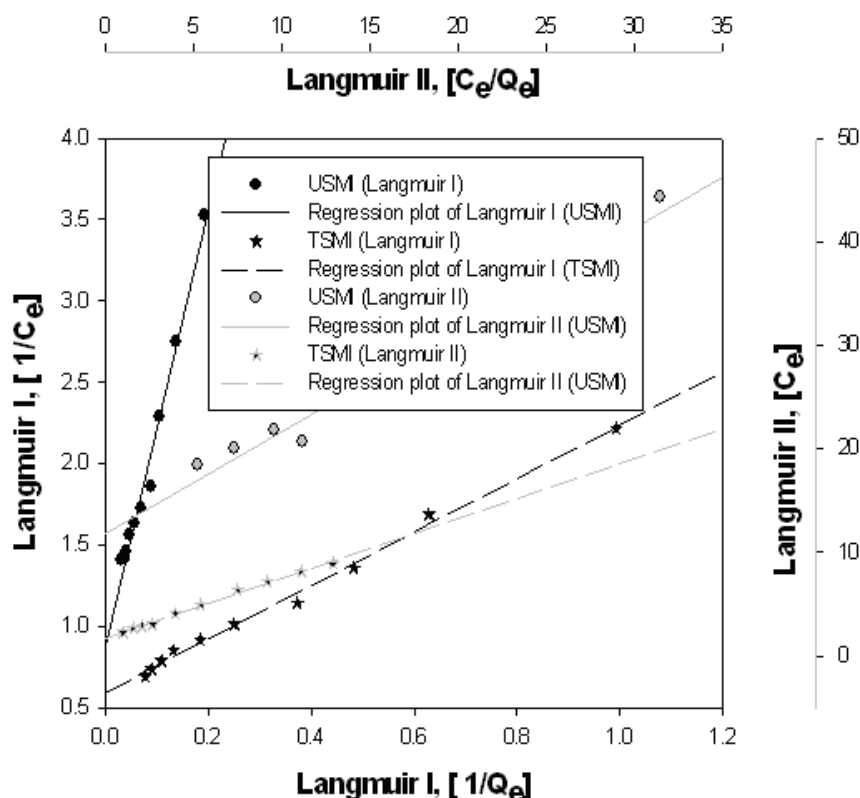


Figure 3: Linearised isotherms of Langmuir Model I & II for both adsorbents. For Langmuir model I, graph is plotted between $1/Q_e$ versus $1/C_e$ and similarly for Langmuir model II, it is plotted in C_e/Q_e versus C_e . Experimental Parameters for both plots; Initial Oil Concentration: from 12.3 mg L^{-1} to 49.2 mg L^{-1} , Adsorbent dose: 25 gm L^{-1} , $pH = 3$, Temperature: 25°C , Agitation speed: 150 rpm and Particle Size: 177-100 μm .

Validation of Adsorption Models

Results of the batch adsorption study and graph plotted on Figure 4 indicate very little variation in predicted data from observed experimental data. Correlation coefficient of experimental data and predicted results of Freundlich and Langmuir Model I & II for oil adsorption are tabulated in Table 3.

Table 3: Correlation Coefficients for Experimental and Observed Data

Adsorption Models	Correlation Coefficients	
	USMI	TSMI
Freundlich	0.966	0.981
Langmuir Model I	0.991	0.994
Langmuir Model II	0.991	0.997

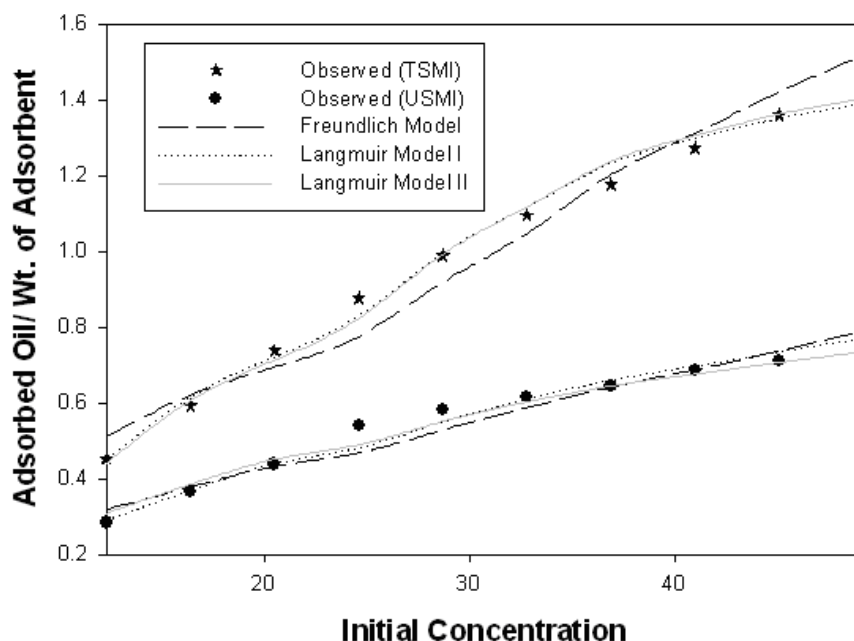


Figure 4: Validation of Freundlich Model, Langmuir Models I & II. Experimentally observed adsorbed emulsified oil per unit weight of adsorbents in mg.gm^{-1} versus initial concentration in mg.L^{-1} of oil has been plotted for TSMI and USMI at Initial Oil Concentration: from 12.3 mg.L^{-1} to 49.2 mg.L^{-1} , Adsorbent dose: 25 gm.L^{-1} , $\text{pH} = 3$, Temperature: 25°C , Agitation speed: 150 rpm and Particle Size: 177-100 μm .

Conclusion

Adsorption results of batch study and numerical analysis of experimental data show little variation in the predicted results of Freundlich and Langmuir theory of adsorption for emulsified oil removal. Correlation coefficient for both models are approaching towards unity indicate the applicability of Freundlich and Langmuir theory for the oil adsorption through sawdust of mangifera indica.

References

- Benito Y, Ruiz ML, (2002) Reverse osmosis applied to metal finishing wastewater. *Desalination*, **142**, 229-234.
- Bethea RM, Duran BS, Boullion TL, (1985) *Statistical Methods for Engineers and Scientists*, Marcel Dekker, Inc, New York.
- Chakraborty S., De S, Gupta SD, Basu JK, (2005) Adsorption study for the removal of a basic dye: experimental and modeling. *Chemosphere* **58**, 1079–1086
- Chakravarty S, Dureja V, Bhattacharyya G, Maity S, Bhattacharjee S, (2002) Removal of arsenic from groundwater using low cost ferruginous manganese ore. *Water Research*, **36**, 625-632.
- Freundlich HMF, (1906) Over the adsorption in solution. *Z. Phys. Chem.* **57**, 385-470.
- Hilal N, Busca G, Hankins N, Mohammad AW, (2004). The use of ultra filtration and nanofiltration membranes in the treatment of metal working fluids. *Desalination*, **167**, 227-238.
- Langmuir I, (1918) The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.*, **40**, 1661-1368.
- Mathavan GN, Viraraghavan T, (1992) Coalescence/filtration of an oil-in-water emulsion in a peat bed. *Water Res.* **26**, 91-98.
- McCoy JS, (1994) *Introduction: Tracing the historical development of metalworking fluids*. In: Byers JP (Ed.), *Metalworking fluids*, Marcel Dekker, New York
- NIOSH, (1998) *Criteria for a recommended standard: occupational exposure to metal working fluids*, US.
- Raji C, Anirudhan TS, (1997) Chromium (VI) adsorption by sawdust: Kinetics and Equilibrium. *Indian J. Chemical Technology*, **4**, 228-236.

- Rao M, Bhole, AG, (2001) Chromium removal by adsorption using fly ash and bagasse. *J. Indian Water Works Association*, XXXIII, **1**, 97-100.
- Rengaraj S, Yeon KH, Moon SH, (2001) Removal of chromium from water and wastewater by ion exchange resins. *J. Hazard. Mater.* **87**, 273-287.
- Solisio C, Lodi A, Converti A, Del Borghi M, (2002). Removal of exhausted oils by adsorption on mixed Ca and Mg oxides. *Water Res.* **36**, 899-904.
- Stumm W, Morgan JJ, (1981) *Aquatic Chemistry*, Wiley Inter science, Second Ed, John Wiley & Sons, New York.
- Viraraghavan T, Mathavan GN, (1990) Treatment of oily waters using peat. *Water Pollut. Res. J. Can.* **25**, 73-90.
- Weber WJ, (1972) In: R.L. Metcalf, J.N. Pitts (Eds.), *Adsorption in Physicochemical Processes for Water Quality Control*, Wiley Inter Science, NY, 199-259.
- Yurlova L, Kryvoruchko A, Kornilovich B, (2002) Removal of Ni (II) ions from wastewater by micellar-enhanced ultra filtration. *Desalination*, **144**, 255-260.