Research Article

Adsorption Soluble Cutting Fluid Emulsion by Modified Chitosan with SLES

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Abstract

This study examined the effect of modifying chitosan (MC) with sodium lauryl ether sulfate (SLES) in adsorbing soluble cutting fluid emulsion (SCFE). The adsorbent was prepared by the addition of SLES to chitosan solution followed by sulfuric acid immersion. Batch adsorption was carried out as a function of initial concentration of the soluble cutting fluid emulsion. The point of zero charge of the adsorbent was also measured at pH 1.9. The percent adsorption was calculated and found out to decrease, whereas the adsorption capacity increases as the initial concentration of the adsorbate increases. Experimental results showed that using 2.0 g of the modified chitosan in a 72,227 mg/L soluble cutting fluid emulsion concentration, a 2,518.8 mg/g adsorption capacity was calculated. Models of Langmuir and Freundlich were applied to describe the adsorption isotherm together with coefficient of determination and chi-square error function calculations. The Langmuir isotherm best fitted the experimental data of the modified chitosan. In addition, the significant uptake of the soluble cutting fluid emulsion was demonstrated by the changes in the FTIR spectra and the heat of combustion of the modified chitosan before and after the adsorption process.

Keywords: Adsorption, Soluble cutting fluid emulsion, Modified chitosan, Adsorption isotherm, Batch design

1 Introduction

Machining is a process wherein it involves metal rod and plate forming and cutting processes. It includes a moving and stationary segments that when in motion, generates friction. This opposing force, in the absence of lubrication, generates a considerable amount of heat between the tool and the workpiece [1]. The tool's surface will wear and lose its strength in addition to the reduced workpiece precision and uniformity. Utilization of metal working fluids or cutting fluids must be employed in order to minimize the effects of friction. With their lubricating and cooling properties, the thermal deformation of the workpiece will lessen, the tool will have an increased resistance to wear, and will help to remove minute particles of the processed metal [2].

Cutting fluid exists in two base forms of oil and water [3]. This oil-based cutting fluid, commonly known as straight oil, was derived from natural and synthetic materials. The natural-derived cutting fluid was obtained from flora, fauna, and aquatic resources while the latter was refined from petroleum. On the other hand, water-based cutting fluid includes soluble, synthetic, and semi-synthetic containing solution which creates an oil-water emulsion. The soluble cutting fluid contains a mixture of mineral oil and emulsifier

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that acts as a surfactant. The synthetic cutting fluid, commonly known as chemical fluid, contains compounds of polyalphaolefins and corrosion inhibitors. Nevertheless, semi-synthetic fluids are a combination of both soluble and synthetic [4].

Prolonged exposure to these fluids, especially soluble cutting fluids, can cause detrimental damage to the welfare of the workers [5]. The soluble cutting fluid contains compounds that serve as a nutrient for bacterial and fungi growth. When inhaled, these pathogens can result to respiratory diseases. Also, skin contact can cause irritation due to the presence of chromium, nickel, or cobalt contaminants. In addition, the presence of heterocyclic and polyaromatic compounds, which can react to atmospheric oxygen, were reported to have carcinogenic abilities [6].

In order to address the aforementioned health issues, various processes have been proposed to treat soluble cutting fluid emulsion. It includes chemical, electrochemical, membrane, thermal, and biological processes. In a chemical treatment, aluminum (III) or iron (III) were used in order to de-stabilize the emulsion and for oil drop enhancement [7]. The electrochemical process uses an electrode and current to reduce the emulsion and for oil drop separation [8]. Moreover, membrane processes use thin porous film to separate emulsion [9] and the thermal treatment involves high operating temperatures to disintegrate complex emulsion compounds [10]. Bacteria were used in a biological treatment to decrease the concentration of organic nutrient of the emulsion [11]. However, these processes are quite selective on the parameters of the emulsion to be treated. The chemical and electrochemical treatments are used only for oil separation at the surface of the effluent wastewater. While thermal and biological processes require large amount of energy and extensive treatment period, respectively.

Another process used for treating wastewater is adsorption which involves the use of adsorbents, the materials used for adsorption, and the adsorbate, the material to be adsorbed. A process that can operate at normal conditions: temperature and pressure. Addition of chemicals for the purpose of cleaning the adsorbent is not a requirement. Moreover, adsorbent saturation will not hinder the treatment process. However, even though adsorption is one of the simplest type of separation technique, its application to the treatment of soluble cutting fluid emulsion was very limited. Mathavan and Viraraghavan used peat in order to adsorb cutting, refinery, crude, and mineral oils [12]. Solisio *et al*., used mixtures of calcium and magnesium oxides as adsorbents to treat exhausted oils [13]. Cambiella *et al*., addresses oil-water emulsion by using sawdust [14]. Piyamongkala *et al*., applied sodium dodecyl sulfate (SDS)-modified chitosan to remove cutting fluids [15]. Many types of adsorbents such as Mangifera indica sawdust [16], powdered lemon peels [17], chitin and chitosan [18], lanthanum coordinated with chitosan flake [19], and lanthanum/chitin and zirconium/chitin composites [20] used to treat soluble cutting fluids emulsion.

Chitosan or poly-(1-4)-2-amino-2-deoxy-β-D-glucose is obtained by chitin deacetylation in a base medium [21]. The presence of amino (-NH_2) and hydroxyl (-OH) groups, positioned at C-2 and C-6 respectively, serves as the active sites for coordination to adsorb wastewater pollutants such as zinc (II), reactive yellow - 145 dye, and/or nitrate and phosphate anions [22]–[24].

Several studies suggests that modifying chitosan matrix by sodium dodecyl sulfate (SDS) molecule can dramatically increase its mechanical and chemical properties [25]. In the literature review of soluble cutting fluid emulsion adsorption, it was found that no working has been done in the previous regarding to adsorb soluble cutting fluid emulsion on modified chitosan with SLES. With these, this paper intends to 1) study the feasibility of using SLES-modified chitosan as an adsorbent to adsorb soluble cutting fluid emulsion, 2) determine the initial concentration of the soluble cutting fluid emulsion that can influence sorption, 3) evaluate isotherms of Langmuir and Freundlich, and 4) evaluate the sorption capacity of the adsorbent.

2 Materials and Methods

2.1 *Preparation of modified chitosan*

Chitosan flakes with a 95% degree of acetylation (average molecular weight of 700,000 daltons) were purchased from Sea Fresh Co., Ltd., Thailand. A 100 cm^3 of 2% by volume aqueous acetic acid was transferred to a beaker followed by the addition of 2.0 g of chitosan flakes. The mixture was then agitated by an overhead stirrer (Janke & Kunkel; Model RW 20) at room temperature for 12 h at 300 rpm producing a viscous

Figure 1: Modified chitosan.

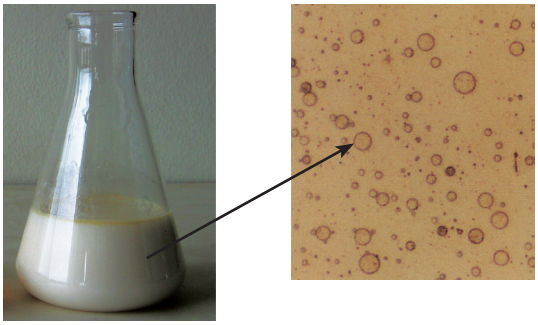

Figure 2: Oil in water of soluble cutting fluid emulsion.

light yellow colored solution.

Chitosan sheet was prepared by injecting 20.0 cm^3 of 50% by volume of sodium lauryl ether sulfate (SLES) solution into 100 cm^3 chitosan solution followed by agitation at 90 rpm for 5 min at room temperature. Excess SLES and acetic acid was washed with fresh water several times. The resulting sheet was immersed in a 0.5 M sulfuric acid for 24 h followed by filtration [26]. Modified chitosan (MC) is shown in Figure 1.

2.2 *Preparation of cutting fluid*

The soluble cutting fluid (commercial grade) was purchased from Rifle Brand Trade Mark, Thailand. It was mixed with water and stirred at 1,200 rpm for 10 min using an overhead stirrer to for a white colored emulsion. The pH of the resulting of emulsion was determined to have a value of 8.9 by a pH meter (Eutech; Model pH 510) after allowing it to stabilize for 10 min. The soluble cutting fluid emulsion (SCFE) is shown in Figure 2.

2.3 *Adsorption process*

All batch adsorption experiments were performed in a 250 cm^3 Erlenmeyer flasks. Two (2.0) g of the adsorbent was added in a 100 cm^3 soluble cutting fluid emulsion (emulsion concentration varies in the range of 2,100–72,225 mg/L) in a flask. The mixture was agitated at 120 rpm at room temperature. Initial and residual concentration of soluble cutting fluid emulsion that was determined at equilibrium were measured using visible spectrophotometer (Thermo electron; Model Spectronic Genesys 20) at 395 nm [15]. The percent adsorption and adsorption capacity at equilibrium was calculated by Equations (1) and (2), respectively.

$$\%\ \text{Adsorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

$$q_{e,\ exp} = \left(\frac{(C_0 - C_e) \times V}{W}\right) \tag{2}$$

where C_0 is the initial concentration and C_e is the equilibrium concentration of the soluble cutting fluid emulsion (mg/L), $q_{e,\ exp}$ is the experimental adsorption capacity at equilibrium (mg/g), V is the volume of the soluble cutting fluid emulsion (L) and W is the weight of the adsorbent (g).

2.4 *Point of zero charge of modified chitosan*

The pH_{pzc} of the modified chitosan was measured by preparing a solution of 0.1 M sodium chloride using a pre-boiled distilled water. One hundred (100) cm^3 of this salt solution was transferred to a 250 cm^3 Erlenmeyer flasks then followed by the addition of either 0.1 M hydrochloric acid or sodium hydroxide to adjust the pH between 1.0–11.0 values. A 0.1 g of the adsorbent was added to the solution. It was sealed using paraffin to avoid air contact and agitated using an orbital shaker (UMAC Scientific; Model UM-S60) at room temperature for 48 h. The resulting solution was filtered using Grade No. 1 filter paper. The final pH was then measured and plotted against the initial pH. The pH value that lies in the 45° line, $pH_{initial} = pH_{final}$ was taken to be the point zero charge of the adsorbent.

2.5 *Fourier transform infrared spectrometer*

The functional groups present in the untreated and modified adsorbent and the soluble cutting fluid were determined using FT-IR spectrometer (Perkin-Elmer; Model 2000). The adsorbents were pulverized, homogenized with potassium bromide, and pelletized for sample preparation. The average of 10 scans were made in a 4,000–400 cm^{-1} range with a resolution of 4 cm^{-1}.

2.6 *Heat of combustion determination*

The heat of combustion of the soluble cutting fluid, before and after the adsorption, was measured using a bomb calorimeter (Parr; Model 1341). The heat of combustion was calculated based on the gross heat of combustion following in Equation (3) [15].

$$H_g = \left(\frac{TE - e_1 - e_2 - e_3}{W} \right) \quad (3)$$

where H_g is the gross heat of combustion (J/g), T is the net corrected temperature rise (K), E is the energy equivalent (heat capacity) of the calorimeter (J/K), On the other hand, e_1, e_2, and e_3 are the correction factors for the heat of formation of nitric acid, sulfuric acid, and the fuse wire (J), respectively.

3 Results and Discussion

3.1 *Point of zero charge*

The point of zero charge of the adsorbent is the pH at which the surface is electrically neutral, i.e., the net charge of the modified chitosan is zero or it possess an equal number of positive and negative charged functional groups. This can be observed by comparing the pH of the solution to the pH of the point of zero charge of the adsorbent [27]. Below this value, the net charge of the adsorbent will be positive otherwise it will be negative. Figure 3 shows the pHpzc drift test of the modified adsorbent and measured to have a value of pH 1.9. The prior immersion of the adsorbent to an acid amplified its efficiency as the acid charged the surface with proton ions. This addition yielded a positive charged surface that can destabilize the negatively charged adsorbate by charge neutralization.

On the other note, the zeta potential of the soluble cutting fluid emulsion was determined to be at pH 3.2 [15]. This was influenced by the presence of organic additives that may vary from anionic to ionic molecules of amine, fatty acid, ester, sulfonate, borate, and/or phosphate.

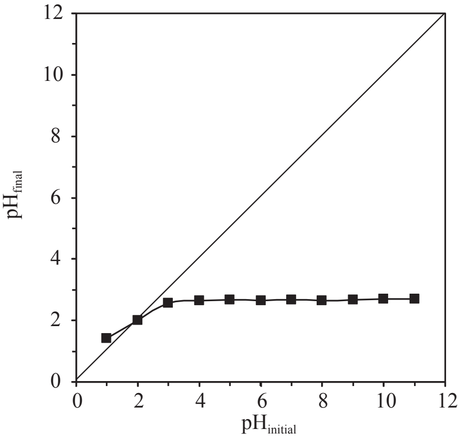

Figure 3: Point of zero charge of modifed chitosan.

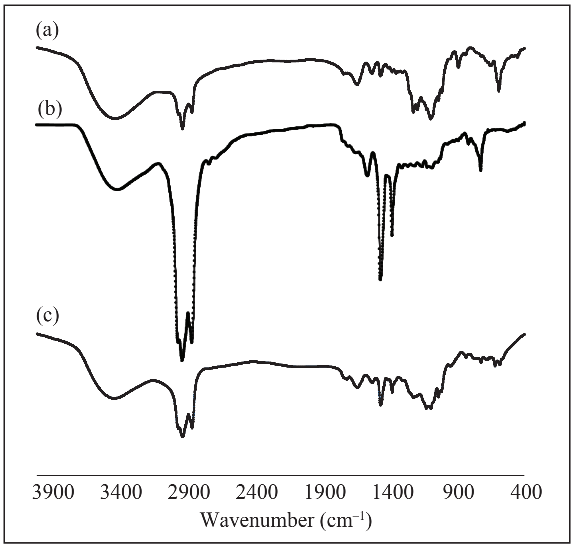

Figure 4: FT-IR spectra: (a) Modified chitosan, (b) soluble cutting fluid and (c) modified chitosan after adsorption.

3.2 *Fourier transform infrared spectroscopy*

The spectra of the modified chitosan before adsorption is shown in Figure 4(a). The presence of an alkane stretch (C-H) was verified by the peaks at 2,923 and 2,857 cm^{-1}. Figure 4(b) shows the spectra for the soluble cutting fluid emulsion [28]. The appearance of peaks at 2,925 and 2,855 cm^{-1} confirmed the presence of an alkane stretch (C-H). The methylene (CH_2),

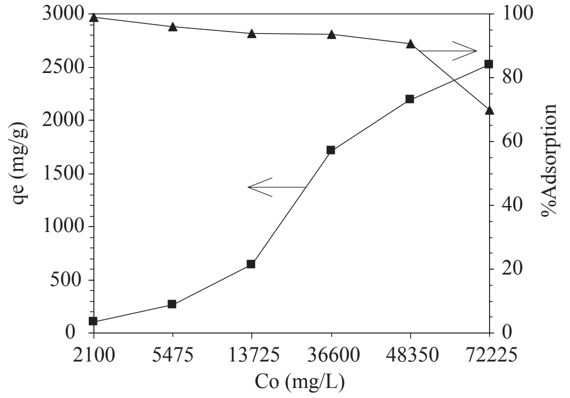

Figure 5: Efficiency adsorption: ▲ % adsorption and ■ adsorption capacity.

methyl (CH_3) and four carbon chained methylene (CH_2 long chain more than four atoms) functional groups were verified by the appearance of 1,465, 1,375, and 720 cm^{-1} peaks. Figure 4(c) shows the spectra of the modified chitosan after the adsorption process. In comparison with Figure 4(a), there are the appearance of peaks at 2,927, 2,869 cm^{-1} and 1,468 and 1,379 cm^{-1} which signifies alkane, methylene and methyl groups, hence, a favorable adsorption outcome; adsorbent adsorbs adsorbate.

3.3 *Effect of initial concentration of soluble cutting fluid emulsion*

The percent adsorption and the adsorption capacity at equilibrium is shown in Figure 5. Increasing the amount of the soluble cutting fluid emulsion resulted to a decrease in the percent adsorption by 99.8–69.7%. This significant drop can be attributed to the saturation capacity of the adsorbent wherein the ratio of the adsorbate molecules to the vacant adsorption sites in the adsorbent were exceeded which was consistent with results using pistachio hull waste for cationic dyes adsorption [29].

The equilibrium adsorption capacity was set within the range of 103.8–2,518.8 mg/g. This adsorption capacity increases with respect to the initial concentration of the soluble cutting fluid emulsion in order to maintain a proportionate ratio of the adsorbate to the adsorbent, thus, maintaining a driving force for adsorption. This correlation is comparable with the results reported on the adsorption of methyl orange and reactive red dyes using *moringa peregrine* ash [30]. The comparison of the adsorption capacities of different modified chitosan as an adsorbents for adsorption of soluble cutting oil emulsion is shown in Table 1.

Table 1: Comparison of adsorbent capacities of different modified chitosan adsorbents

MC	q_e (mg/g)	Reference
SDS	2,500.0	[15]
BE-MC-SDS	2,922.5	[31]
SLES	2,518.8	This research

3.4 *Adsorption isotherm*

Adsorption isotherms were used in order to evaluate the variation between experimental and theoretical adsorption processes [32]. In this paper, Langmuir and Fruendlich adsorption isotherm were used [33]. The non-linear and linear forms of the Langmuir isotherm were represented by Equations (4) and (5), respectively.

$$q_{e,\,cal} = \frac{a_{m,L}\, C_e}{1 + K_L\, C_e} \tag{4}$$

$$\frac{C_e}{q_{e,exp}} = \left(\frac{K_L}{a_{m,L}}\right) C_e + \frac{1}{a_{m,L}} \tag{5}$$

where $q_{e,cal}$ is the calculated adsorption capacity at equilibrium (mg/g), $a_{m,L}$ is the Langmuir isotherm constant (L/g), and K_L is the free adsorption energy based Langmuir constant (L/mg).

Simultaneously, the non-linear and linear forms of the Fruendlich isotherm were represented by Equations (6) and (7), respectively.

$$q_{e,\,cal} = K_F C_e^{\,1/n} \tag{6}$$

$$log\ q_{e,\,exp} = log\ K_F + 1/n\ log\ C_e \tag{7}$$

where K_F is the Freundlich constant [(mg/g)(L/mg)$^{1/n}$] and 1/n is the heterogeneity factor (dimensionless).

The coefficient of determination, R^2 of the Langmuir and Freundlich isotherms are shown in Figures 6 and 7, respectively. The values for the calculated $a_{m,L}$, K_L, K_F, and n was presented in Table 2.

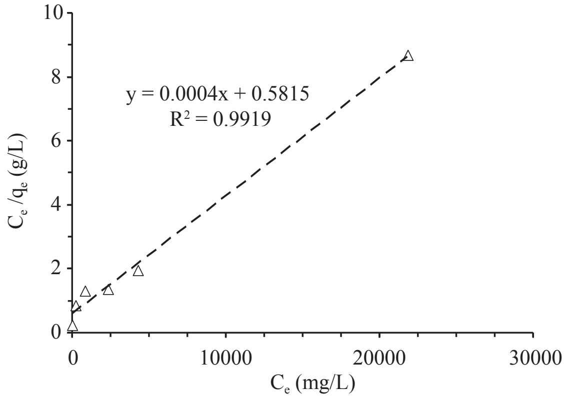

Figure 6: Langmuir adsorption isotherm.

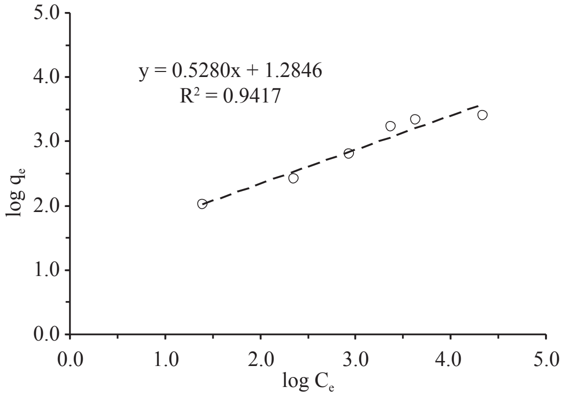

Figure 7: Freundlich adsorption isotherm.

The Langmuir and Freundlich isotherm curves are presented in Figure 8. It was determined that the best fit for the calculated data was the Langmuir isotherm. In addition, the coefficient of determination of the Langmuir isotherm was higher than that of the Freundlich isotherm, thus, consistency of the results

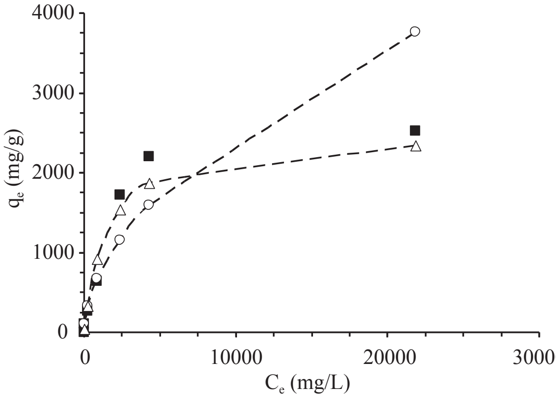

Figure 8: Equilibrium adsorption: ■ experimental, △ Langmuir and ○ Freundlich.

were obtained from the experiment. The correlation will give a better fit to higher C_e data points which is an inherent bias in the linearized isotherm plots [34]. Due to the presence of this bias, chi-square (χ^2) error function was calculated to evaluate the isotherm constant and to aid the selection of the best fit isotherm. This error function can be calculated using Equation (8) [35].

$$\chi^2 = \sum \left(\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right) \tag{8}$$

The values of chi-square were also presented in Table 2. Comparing the calculated error function of both isotherms, it suggests that the best fit isotherm was the Langmuir since it has a relatively low error value. In lieu of this, the porous surface of the modified adsorbent contributed to the adsorption of the soluble cutting fluid emulsion.

Table 2: Langmuir and Freundlich constants of soluble cutting fluid emulsion sorption onto modified chitosan

SCFE (mg/L)	**$q_{e,\,exp}$ (mg/g)**	**Langmuir Isotherm**					**Freundlich Isotherm**				
		$a_{m,\,L}$ (L/g)	**K_L (L/mg)**	**R^2**	**χ^2**	**$q_{e,\,cal}$ (mg/g)**	**n**	**K_F (mg/g)(L/mg)$^{1/n}$**	**R^2**	**χ^2**	**$q_{e,\,cal}$ (mg/g)**
2,100	103.8	1.72	0.00069	0.9919	258.8	42.3	1.89	19.26	0.9417	991.7	105.4
5,475	262.5					335.1					336.2
13,725	643.8					922.4					678.2
36,600	1,725.6					1,544.5					1,160.2
48,350	2,202.5					1,868.3					1,596.1
72,225	2,518.8					2,344.0					3,765.6

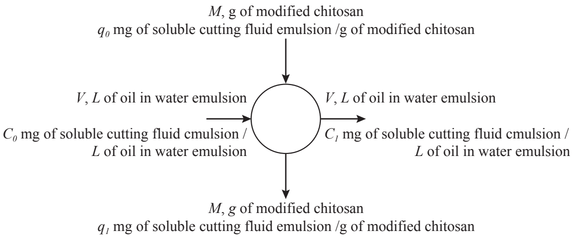

Figure 9: Single stage batch adsorption.

3.5 *Batch design*

Adsorption isotherm relations were used to predict the design of the single-stage batch adsorption system [36], [37]. The schematic diagram for a single-stage batch adsorption system is presented in Figure 9. An inlet stream of the emulsion, V is supplied to the volume of adsorbate with an initial concentration of C_0 that will be reduced to its final concentration of C_1 by another inlet stream of the modified chitosan, M with a mass of adsorbent, q_0 which in turn increase its value to q_1 after the adsorption process. Applying a mass balance, with the assumption of q_0 value to be zero, the mass of the soluble cutting fluid emulsion removed from the emulsion will be the mass of the adsorbate attached to the surface of the adsorbent, thus, the equation for this sorption system can be written as Equation (9) [36].

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \tag{9}$$

At equilibrium condition, the following parameters will be transformed into Equation (10).

$$C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e \tag{10}$$

Since the best fit curve is determined to be the Langmuir isotherm, Langmuir data will be used in Equation (9) followed by the substitution of the q_e term in Equation (4). Rearranging was displayed in the Equation (11).

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{\left(\dfrac{1.72\,C_e}{1+(0.00069C_e)}\right)} \tag{11}$$

The Equation (11) allows the analytical calculation of the modified chitosan ratio for a given change in soluble cutting fluid emulsion concentration, C_0 to C_1. A plot derived for Equation (11) is shown in Figure 10 having a 69.7% adsorbate removal. Having these, a liter of soluble cutting fluid emulsion will require 0.03 g of the modified chitosan.

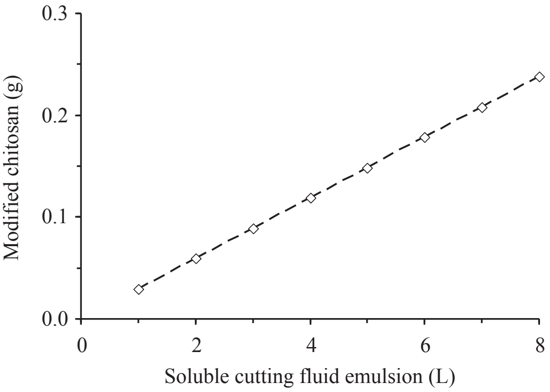

Figure 10: Amount modified chitosan vs. volume soluble cutting fluid emulsion.

Having known the volume of the adsorbate and the amount of the adsorbent, the construction of the adsorption operating line was based from Equation (11) [38]. The adsorption capacity is displayed as Equation (12).

$$q_{e,\,cal} = \frac{V}{M}(C_0 - C_e) \tag{12}$$

Equation (12) was used in order to calculate the concentration of the soluble cutting fluid emulsion at equilibrium. The equilibrium condition of the adsorption process is shown in Figure 11. The equilibrium concentration of 22,000 mg/L for soluble cutting fluid emulsion and equilibrium adsorption capacity of 2,600 mg/g was predicted by the intersection of the equilibrium line with the operating line.

The removal of soluble cutting fluid emulsion and the required amount of the modified chitosan are calculated using Equations (13) and (14), respectively. [39].

$$SCFE\ removal = Q(C_0 - C_e) \tag{13}$$

$$MC\ required = \frac{SCFE\ removal}{q_{e,exp}} \tag{14}$$

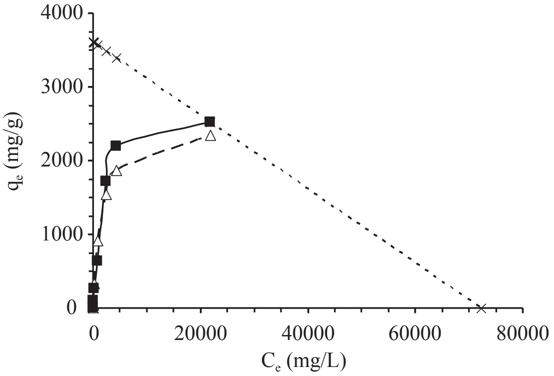

Figure 11: Operation line adsorption:■ experimental, △ Langmuir and × operating line.

where Q is the industrial wastewater flow rate of the soluble cutting fluid emulsion (m^3/h).

With Q equal to 1 m^3/h, the computed adsorbate removal rate and required adsorbent are 50.4 kg/h and 20.0 kg/h, respectively.

3.6 *Heat of combustion*

A change in the value of the heat of combustion of a material indicates a variation with its physical or chemical properties. In this experiment, the heat of combustion of the modified chitosan significantly increased to 22.1 kJ/kg from an 18.6 kJ/kg after the adsorption process. The difference between these values arise from the adsorption of adsorbate molecules. Considering the final value for the heat of combustion, the modified chitosan after the adsorption process can be used as a solid fuel.

4 Conclusions

The modified chitosan is an effective adsorbent for soluble cutting fluid emulsion. Through series of experimentation, the adsorption capacity was found to increase with respect to the initial concentration of the soluble cutting fluid emulsion. Also, the Langmuir isotherm was determined to be the best fit model based from the values of coefficient of determination and chi-square error function. The sorption capacity of the adsorbent was determined to have a value of 2,518.8 mg/g using 2.0 g of the modified chitosan and 72,227 mg/L for the initial concentration value of the soluble cutting fluid emulsion.

Acknowledgments

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