Soluble oil adsorption onto modified chitosan beads

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Abstract. The adsorption soluble oil emulsion was studied in the laboratory scale. The effect of initial concentration of soluble oil to adsorb onto the surface of modified chitosan beads with 0.25 M hydrochloric acid solution was investigated. It was found that the maximum adsorption capacity soluble oil onto modified chitosan beads was 10,000 mg/g. The proton from hydrochloric acid which using as modified showed the role to destabilize soluble oil. The adsorption isotherm corresponded to the Langmuir equation.

1 Introduction

Metal working fluid (MWF) is a commonly group of lubricants that is used in the metal processing of turning, planing or drilling which creates heat from friction between cutting tool and workpiece. If a cooling is not done very well that causes the wear of cutting tool. As a result, the workpiece has an uneven surface. Therefore, MWF is used to reduce friction, cooling and washes away metal scraps. MWF can be divided into 4 types as follows: straight oil, soluble oil, semisynthetic oil and synthetic oil [1]. The last three types are suitable for forming metal workpieces that use at high speed spinning. High specific heat capacity of water is played a big role in quickly reducing a temperature from friction. While using water to dilute the concentration of fluids can cause important problems, including corrosion at a surface of the metal workpiece and good growth of bacteria in water. Therefore, additives must be added to increase efficiency, including anti-corrosion substances, microbial control substances, anti-foaming agent, rust inhibitor, buffering agents, dispersion aids and stabilizers, etc [2].

Soluble oil is used widely popular in a metal fabrication industry because it has highly stable, good lubrication and excellent cooling efficiency. It is suitable for machining heavy-duty metal workpieces at high speeds and also cheap. After using, soluble oil loses lubricating properties and forms toxic waste in the water. Danger is arisen from contamination by bacteria and fungi that causes respiratory disease. The new chemicals can be appearance for the additives that react with air during friction. When workers are exposed or immersed in soluble oil for a long time, they are easy to cause skin rashes [3]. Releasing soluble oil into public water sources therefore has an adverse effect that causes a major wastewater problem.

Soluble oil treatments include evaporation, microwave radiation, precipitation, membranes and electrolysis [4]. All methods as mentioned above that provide high treatment efficiency but have limitations and disadvantages as follows; requires energy to operate, causes harm to workers due to radiation exposure, encounters problems with block at surface membrane, polluted of sludge in sedimentation and has a high operating cost, respectively [5]. Therefore, choosing a treatment method to treat soluble oil must be necessary to consider the amount of energy used, chemical hazards and cost of maintaining the wastewater treatment system. While adsorption is an effective process for treating soluble oil. It has important advantages that includes to use low energy, carried out at atmospheric temperature and pressure, takes a short time, doesn't need to add chemicals, so it is highly safe. The adsorbent can be used natural materials or agricultural waste, making the investment cost dose not too high [6].

Chitin is found mainly in the shells of shrimp, crabs, and insects. It is also found in the cell walls of some fungi and algae [7]. Chitosan is produced by the reaction of removing the acetyl group in chitin with a concentrated alkaline solution. The structure of chitosan with amino groups is considered a positively charged natural polymer. Its important outstanding properties include being biodegradable and non-toxic [8]. Chitosan is widely applied as follows; in the medical and pharmaceutical fields is used a natural substance that can be eaten. Therefore, chitosan has been utilized in drug delivery systems and wound dressings. In terms of agriculture, chitosan is used to control the release of minerals, nutrients for plants and control the evaporation of water at the soil surface [9]. In the area of the environment, chitosan has been applied as an adsorbent for pollutants in wastewater for example to adhere well to dyes, heavy metals, or toxic chemicals [10].

This research, a highly efficient absorber was invented with simple process, low hazard and shallow concentration of chemicals, carried out at atmospheric temperature and pressure, using a little energy and low cost. The adsorbent showing in form of beads was developed commercially and able to reduce the impact on the environment and water pollution very well.

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2 Materials and methods

2.1 Preparation modified chitosan beads

Commercial grade chitosan powder (93 % degree of deacetylation from shrimp shell) was purchased from The Sin Udom Co., Ltd., Thailand. To prepare the chitosan solution, 30 g of chitosan powder was dissolved in 1,000 cm^3 of 4 % v/v dilute acetic acid, then stirred by overhead stirrer at 200 rpm for 8 h and left the mixture for 72 h to obtain clear yellow solution and highly viscosity of chitosan. To provide chitosan beads, the chitosan solution was sucked by the peristaltic pump, moved into the small diameter of rubber tube (Ø1.6 mm.) and dropped through the needle at flow rate 2.9 cm^3/min into 1,000 cm^3 of 20%w/w sodium lauryl ether sulfate solution, then left for 72 h to obtain hard beads. The hard beads were washed by tap water for remove excess of sodium lauryl ether sulfate and dried in sunlight to obtain the chitosan beads. To bracket modified chitosan with hydrochloric acid solution, 4 g of chitosan beads soaked in 100 cm^3 of hydrochloric acid solution at 0.25 M and stirred by orbital shaker at 120 rpm for 24 h, then filtered with sieve and dried in the sunlight to obtain the modified chitosan with hydrochloric acid beads, as shown in Fig. 1 (a).

2.2 Arrangement soluble oil

Industrial grade soluble oil purchased from The Rifle Brand Trade Mark, Thailand. To get soluble oil emulsion, 10 g of soluble oil mixed with 1000 cm^3 of distilled water and stirred by overhead stirrer at 1,210 rpm for 10 min to demonstrate white color of oil in water emulsion which was shown in Fig. 1 (b). The pH of emulsion was measured by pH meter and displayed at pH 8.90.

2.3 Adsorption experiments

Batch adsorption experiments of lab scale size were done in erlenmeyer flasks for 250 cm^3. 2 g of the modified chitosan beads was added in 100 cm^3 of soluble oil emulsion when very initial concentration 4,640, 8,340, 14,490, 24,690 and 35,790 mg/L, then the flasks were shaken by orbital shaker at 120 rpm for 3 h. At equilibrium of adsorption, the emulsion was taken to determine the residual soluble oil concentration. The initial and residual soluble oil concentration was analysed by visible spectrophotometer at 395 nm [11]. The adsorption capacity of soluble oil at equilibrium was calculated using to Eq. (1).

$$q_{e,exp} = \left(\frac{(C_0 - C_e) \times V}{W}\right) \quad (1)$$

where $q_{e,exp}$ is the experimental adsorption capacity of soluble oil at equilibrium (mg/g), C_0 is the initial soluble oil concentration (mg/L), C_e is the equilibrium soluble oil concentration (mg/L), V is the volume of the soluble oil (L) and W is the weight of the modified chitosan beads (g)

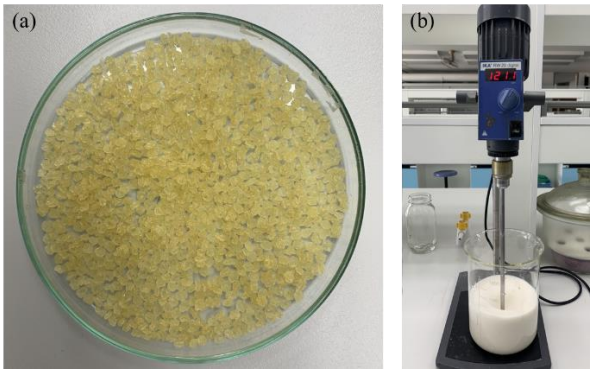

Fig. 1. Photographs of (a) modified chitosan beads and (b) soluble oil preparation

3 Result and discussions

3.1 Adsorption soluble oil

Using 2.0 g of modified chitosan beads to absorb soluble oil 100 cm^3, shaker at the speed of 120 rpm for 3 h, which initial concentrations of soluble oil were 4,640, 8,340, 14,490, 24,690 and 35,790 mg/L, as shown in Fig. 2. It was found that the adsorption capacity of soluble oil at equilibrium of modified chitosan beads were 232, 417, 724, 1,234 and 1,727 mg/g, respectively. The ability to absorb soluble oil of modified chitosan beads tended to enhance with increasing the initial concentration of soluble oil because increasing the initial concentration of soluble oil expanded the driving force from the difference between soluble oil in emulsion and at the surface of modified chitosan beads, thus the adsorption capacity of soluble oil onto modified chitosan beads were boosted by increasing the initial concentration of soluble oil. It was consistently with the research of Aljeboree, et al. used activated carbon to adsorb dye [12]. The modification with hydrochloric acid resulting modified chitosan beads showed the positive charge to destabilized the negative charges of soluble oil [11]. Which was accordingly with the experiment of Tan et al. [13] whose modified activated carbon from coconut shells with hydrochloric acid.

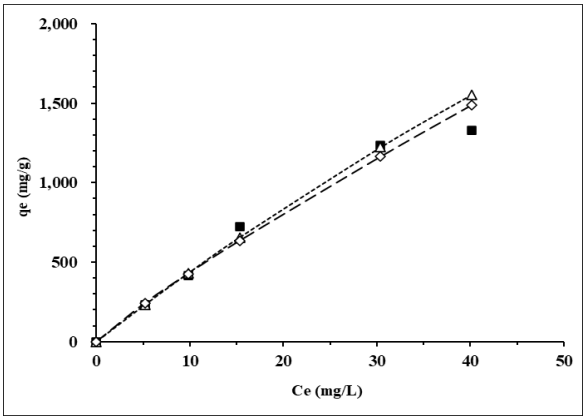

Fig. 2. Adsorption capacity of soluble oil onto modified chitosan beads: ■ experimental, Δ Langmuir isotherm and ◊ Freundlich isotherm

3.2 Adsorption isotherm

The adsorption isotherm is the mathematical equation which used to simulate the adsorption capacity of soluble oil onto the surface of modified chitosan beads by expressing the relationship between the amount of soluble oil attached to the surface of modified chitosan beads. The adsorption capacity of soluble oil at equilibrium (q_e) was presented in the vertical axis and equilibrium soluble oil concentration in the emulsion (C_e) was displayed at the constant temperature in the horizontal axis.

3.2.1 Langmuir isotherm

Predicting the adsorption capacity of soluble oil for Langmuir isotherm can be written as the linear equation and calculated the adsorption capacity value according to Langmuir isotherm from Eq. (2) and (3), respectively [14].

$$\frac{1}{q_{e,\,exp}} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \quad (2)$$

$$q_{e,cal} = \frac{q_m K_L C_e}{1+K_L C_e} \quad (3)$$

where K_L is the Langmuir adsorption constant (L/mg), q_m is the maximum adsorption capacity soluble oil of modified chitosan beads (mg/g) and $q_{e,cal}$ is the adsorption capacity soluble oil of modified chitosan beads from calculation at equilibrium (mg/g)

The experimental result was presented to plot the graph between $1/q_{e,\,exp}$ and $1/C_e$ according to Eq. 2. The result in a straight line of graph was the slope that equaled $1/K_L q_m$ and the intersection point of line was $1/q_m$, as shown in the Fig. 3.

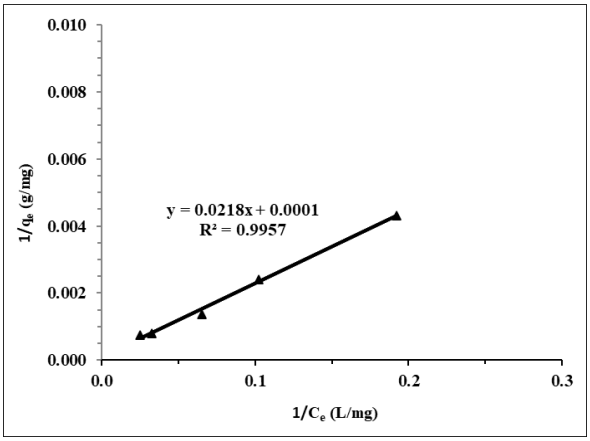

Fig. 3. Linear plot Langmuir adsorption isotherm

3.2.2 Freundlich isotherm

Prediction the adsorption capacity using the Freundlich isotherm can be written as the linear equation and calculated the adsorption capacity value according to Freundlich isotherm from Eq. (4) and (5), respectively [14].

$$log\, q_{e,\,exp} = \frac{1}{n} logC_e + logK_F \quad (4)$$

$$q_{e,exp} = K_F C_e^{1/n} \quad (5)$$

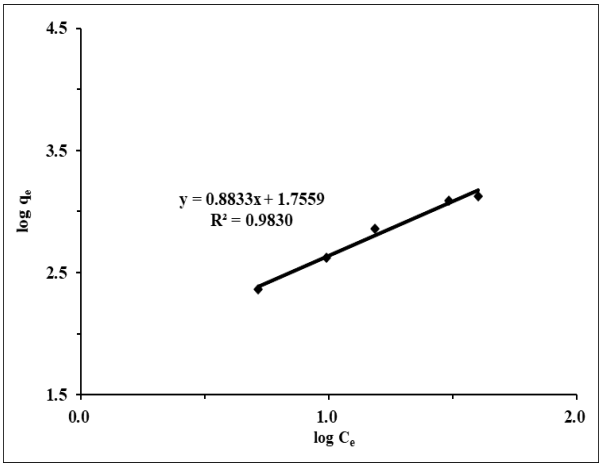

Fig. 4. Linear plot Freundlich adsorption isotherm

where K_F is Freundlich adsorption constant $(mg/g)(L/mg)^{1/n}$ and 1/n is the Freundlich adsorption constant that describes the adsorption concentration and the difference at the modified chitosan beads surface (no units)

The experimental result was displayed again to plot the graph between $\log q_{e,\,exp}$ and $\log C_e$ according to Eq. 4. The end result in a straight line of graph was the slope that equaled 1/n and the intersection point of line was $\log K_F$, as shown in the Fig. 4.

The describing results of the study from the Langmuir and Freundlich equations for the adsorption of soluble oil onto modified chitosan beads to present the values of q_m, K_L, K_F, 1/n and R^2 of both isotherms are shown in Table 1.

Table 1 The adsorption isotherm constants of Langmuir and Freundlich isotherm

C_o	$q_{e,\,exp}$	Langmuir isotherm				Freundlich isotherm			
(mg/L)	(mg/g)	q_m	K_L	R^2	$q_{e,\,cal}$	K_F	1/n	R^2	$q_{e,\,cal}$
4,640	232				232.0				244.5
8,340	417				430.2				428.0
14,490	724	10,000	0.0046	0.9957	655.8	57.0	0.8833	0.9830	634.4
24,690	1,234				1223.8				1163.4
35,790	1,727				1553.7				1485.8

The appropriate adsorption isotherm considered from relative coefficient (R^2). It was found that to be more consistent with the Langmuir isotherm than the Freundlich isotherm. It explained that the adsorption soluble oil onto modified chitosan beads occurred in monolayer [15]. The results of the prediction of adsorption capacity of soluble oil onto the surface of modified chitosan beads according to the Langmuir and Freundlich equations were presented in Table 1.

4 Conclusion

The adsorption capacity of emulsion on the modified chitosan beads was increased by increasing the initial concentration of soluble oil. The adsorption isotherm fitted very well for Langmuir isotherm which showed the soluble oil to adsorb on the surface of modified chitosan beads follow as monolayer and displayed the maximum adsorption capacity at 10,000 mg/g. After the adsorption, the adsorbent can be used as a solid fuel very well.

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