Comparison between supercritical carbon dioxide extraction and aqueous surfactant washing of an oily machining waste

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Abstract

Mathematical models are developed to compare aqueous surfactant washing to supercritical carbon dioxide $(SCCO_2)$ extraction. These two cleaning processes are potentially competitive technologies which can be used to remove oily contaminants from a solid waste. In both processes, the cleaning efficiency for a batch of waste is evaluated by quantifying the residual oil content in the treated sample. A mass transfer model is used to simulate a semi-continuous washing process, and the experimental data, obtained in a batch operation, are used to estimate the equilibrium parameters in the model. For $SCCO_2$ extraction, a linear desorption model is used to describe the supercritical desorption of oil from the solid phase into the CO_2 phase and the simulated results agreed very well with the experimental data. The oil removal in aqueous surfactant washing is viewed to be controlled primarily by the diffusional transport of oil from the interiors of the waste elements to the surface, thus, it can be significantly affected by the size of the particles. A pre-cleaning pulverization is then recommended to improve the cleaning efficiency without increasing any other operation costs. In $SCCO_2$ extraction, the desorption of oil from the solid waste is the controlling step and consequently, the solvent flow rate has no influence on oil removal. Our theoretical studies show that the difference between the cleaning efficiencies of these two technologies is not significant, with the oil concentration in the washing products approximately 5% lower than that in the extraction products. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Oily machining waste; Aqueous surfactant washing; $SCCO_2$ extraction; Diffusion; Desorption

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1. Introduction

Research is in progress to determine the feasibility of separating and recycling the valuable constituents of a solid waste stream which is generated by a South Carolina industry. The solid waste is produced in the high speed tool steel industry when grinding alloy steel to net shape. The waste contains fine $(1-10 \mu m)$ non-porous metal particles as well as porous non-metallic particulates (e.g. from the grinding media), and is covered with a layer of adsorbed cutting oil. This waste is presently all landfilled which poses an environmental pollution problem as well as a loss of raw materials. A successful process for recycling this waste would not only eliminate a large quantity of solid waste but also lead to great savings in materials.

A complete recovery and recycling process for this waste would involve several steps, but removing the adsorbed oil from the solid is one essential step. Therefore, the present paper will focus on oil removal. Two techniques are being evaluated: (1) aqueous surfactant washing, and (2) supercritical carbon dioxide ($SCCO_2$) extraction. These two approaches are potentially competitors for removing organic contaminants from certain solid matrices. Aqueous surfactant washing is a rapidly growing technology which has found extensive application in the cleaning of oily residues from discrete parts. Carman's invention [1] is directed to a method for removing cutting lubricant residues from turnings, borings, mill scales, and grinding byproducts (which are generally referred to as swarf), by washing them with an aqueous detergent solution. Aqueous washing has also been explored for the removal of hydrocarbon contaminants from soils [2–5]. $SCCO_2$ extraction has been promoted for parts cleaning and soil remediation and is considered a promising new technique for hazardous waste clean-up. The ability of $SCCO_2$ to solubilize heavy molecular weight organics is well-documented. Brady et al. [6] used $SCCO_2$ extraction to remove 90% of polychlorinated biphenyls (PCBs) from the contaminated soil. A soil containing over 0.1% polycyclic aromatic hydrocarbons (PAH) was treated by $SCCO_2$ and a 7 h extracting period resulted in the removal of 92% of the contaminant [7]. Another research group also studied the effect of pressure, temperature, and extraction time on $SCCO_2$ extraction of PAH from contaminated land samples and concluded that extraction time was the variable which would significantly affect PAH recovery [8]. Hawthorne et al. [9] examined some extraction processes where the extraction rates of solutes from samples were primarily controlled either by the solubility of the solutes or by the kinetics of the desorption step. In the solubility controlling case, the extraction rates showed direct correlation with fluid flow rates so doubling the solvent rate would double the extraction rate. However, if the process was controlled primarily by the desorption, the extraction rates would show no change with different solvent flow rates.

Even though aqueous surfactant washing and $SCCO_2$ extraction are both applicable to cleaning the oily machining waste, these two methods have different application requirements and cleaning mechanisms. Aqueous washing is a low-pressure process involving the use of specialty surfactant packages, and recovery of water and surfactant is an important consideration. $SCCO_2$ extraction is recognized as a feasible method for removal of certain solutes from solid matrices such as soils and adsorbents. The most notable attractive features of this technique are that CO_2 leaves no residue on the
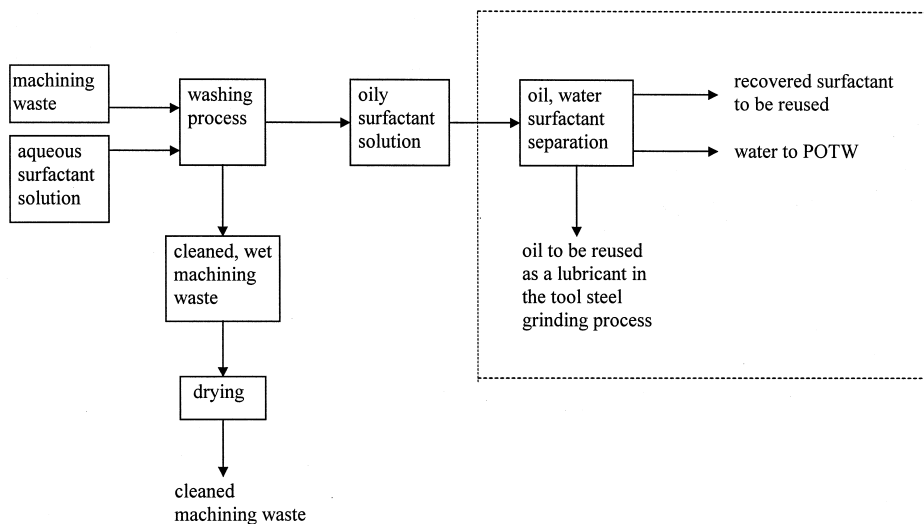
Fig. 1. Flow chart for the aqueous washing process.

processed solid, and the recovery of solute and solvent for reuse can be fulfilled upon a simple expansion to atmospheric pressure. However, $SCCO_2$ requires high-pressure equipment and is not as familiar a technology as surfactant washing.

Both experimental and computational work is in progress to develop an oil removing procedure to clean up the machining waste where $SCCO_2$ extraction and aqueous surfactant washing are employed separately in a semi-continuous cleaning process. The conceptual flow charts of these two cleaning procedures are depicted in Figs. 1 and 2. Although the oil/water/surfactant separation step in Fig. 1 is not part of this paper, one should keep in mind that this step has to be taken into consideration when using aqueous surfactant washing in larger scale applications.

For the present study, bench scale experiments are conducted to determine the optimum operating conditions for oil removal. The experimental data are also used to
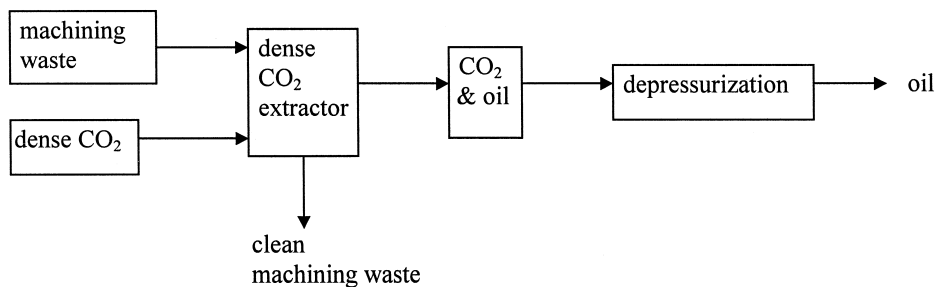
Fig. 2. Flow chart for the $SCCO_2$ extraction process.

estimate the values of some of the model parameters and to test the suitability of the models. Mathematical modeling is needed to generalize the experimental results, to obtain process information which is difficult or impractical to obtain through direct measurement, and to speed up the design process. Additionally, computational studies can also provide information to improve larger scale operations which can result in huge savings with regard to pump size, tankage for contaminated water and surfactant, energy and labor. This paper focuses on theoretical models for describing the oil removal procedure. The mechanisms of the two cleaning processes are described and the simple, generic mathematical models are presented.

2. Mechanisms of aqueous cleaning

The effectiveness of aqueous surfactant cleaning in removing oil from a solid surface is closely related to the ability of the surfactant to solubilize the water-insoluble oil [5]. There are two general mechanisms by which surfactants can enhance the removal of oil from solids, namely *mobilization* and *solubilization.*

The mobilization of oil molecules depends on the tendency of surfactants to reduce the capillary forces (i.e. surface tensions). In solid waste, oil tends to cling to the structure because of surface tension. The effect of surfactants is to allow the aqueous phase to wet the solid surface preferentially. The reduction in surface tension of aqueous surfactant solution can displace oil molecules trapped in the waste that cannot be displaced by water. This can also increase the detergency of the solution by enhancing its ability to disperse and transport oil molecules which would help these molecules to solubilize into the surfactant micelles.

The more important mechanism is solubilization of oil in surfactant micelles. Surfactants are amphiphilic compounds, possessing both hydrophobic hydrocarbon tails and hydrophilic polar heads. As the surfactant concentration approaches the critical micelle concentration (CMC, the surfactant concentration at which micelles first start to form), the hydrophobic tails of the surfactant monomers associate with one another to form micelles consisting of a hydrophobic core surrounded by a hydrophilic mantle. This non-polar interior of a micelle may dissolve substantial quantities of non-polar solutes which are virtually insoluble in normal aqueous solutions, due to the affinity of the oils for the hydrophobic core.

3. Experimental procedure

In our lab, small scale batch cleaning has been performed to evaluate aqueous surfactant washing used to remove oil from the solid waste. The cleaning procedure includes washing, decanting, and drying. About 10 g of the machining waste is added to freshly prepared surfactant solution in a beaker and stirred on a magnetic stirrer for 30 min. The surfactant concentration and the solid to solution ratio are varied for each specific surfactant and for each solid sample. For this paper, we used 2 vol.% surfactant solution to wash the grinding waste and the solid to solution ratio was 10 g:300 ml.

Table 1
Equilibrium results of 30-min batch washing

W_{batch} (g)	V_{batch} (l)	m_0 (g oil/g waste)	m_e (g oil/g waste)	C_e (mol oil/l of solution)
10	0.3	0.2123	0.1500	0.0144

After settling for 30 min, the oily solution was decanted, and the treated waste in the beaker was rinsed twice with tap water to remove the surfactant residue since it can interfere with the analysis of the residual oil. The wet solid was then spread in a flat pan and dried slowly in a furnace at 35–40°C. During the whole procedure, the waste was handled properly with minimum exposure to air, thus oil evaporation could be neglected.

For a batch washing involving small quantity of fine solid matrix, it is reasonable to assume that the oil can come to equilibrium between the aqueous and the solid phases [5]. Our experiments prove that a 30 min washing is sufficient for the oil to reach its equilibrium distribution between the solution and the waste. Longer washing time does not improve the oil removal. Therefore, the residual oil concentration in a washed sample is considered as its equilibrium concentration under the washing conditions. The oil concentration in a solid sample is calculated based on the Total Organic Carbon (TOC) analysis performed by Galbraith Laboratories (Knoxville, TN).

The mass balance for this batch process is:

$$m_0 W_{batch} = m_e W + M_{oil} C_e V_{batch} \tag{1}$$

where C_e (mol oil/l of solution) and m_e (g oil/g waste) are the equilibrium concentrations of oil in solution and in the solid waste, respectively. m_0 (g oil/g waste) is the initial oil concentration in the untreated waste. M_{oil} is the molecular weight of oil, W_{batch} (g) is the amount of waste washed in one batch, and V_{batch} is the volume of solution used. Table 1 shows the results of our batch washing.

Our batch experimental results show that even though the machining waste can be washed to an acceptable level of oil, the desired cleanness cannot be reached in one 30 min washing. A multistage washing process is required. An alternative design, a semi-continuous washing process, might be more suitable for industrial application where the inconvenience and high labor cost of batch operations can be greatly reduced.

4. Mathematical modeling for aqueous surfactant solution cleaning

4.1. A mass transfer model

For modeling purposes, consider a simple semi-continuous cleaning process wherein the machining waste particles are confined in a well-stirred tank and are washed by a continuous flow of oil-free surfactant solution that is charged into the tank from the

bottom. This is a typical unsteady-state process where the oil concentration histories in the solid waste and in the surfactant solution will be needed for the design of washing apparatus and downstream treatment equipment.

First, consider mass balances on the solid phase and on the bulk surfactant solution. Assume that the mass of (oil-free) solid is constant during the washing process, as is the volume of surfactant solution in the washing equipment. Then, the total mass balance for the oil (treated as a single component) in the tank is just a function of time which is given by:

$$M_t = m_t W + M_{oil} C_t V \tag{2}$$

where at time t, C_t (mol/l) is the oil concentration in the solution, m_t (g/g waste) is the oil concentration in solid waste, M_t (g) is the total mass of oil in the tank, and V is the volume of the solution in the tank.

The surfactant solution being charged into the washing tank is free of oil, so the dynamic response of oil mass in the tank is:

$$\frac{dM_t}{dt} = -M_{oil} Q C_t \tag{3}$$

where Q (l/min) is the volumetric flow rate of the surfactant solution.

When the solid involved in the washing operation is in the form of very small particulates which are fluidized by the moving solution, it is reasonable to assume that there are no spatial concentration gradients in the solid bed which means it can be treated as one compartment. We represent the diffusional transport of the oil from the interiors of the solid bed by means of a mass transfer model:

$$\left(\frac{dm_t}{dt}\right)_{diff} = \lambda(m_t^e - m_t) \tag{4}$$

where m_t^e (g oil/g solid) is the equilibrium concentration of oil in the solid waste at time t, and λ (s^{-1}) is the overall mass transfer coefficient within the solid.

We consider a short time interval Δt, then Eq. (4) becomes

$$m_{t+\Delta t} = m_t^e + (m_t - m_t^e)\exp(-\lambda\Delta t). \tag{5}$$

This yields

$$m_{t+\Delta t} - m_t = (m_t^e - m_t)[1 - \exp(-\lambda\Delta t)]. \tag{6}$$

Hence, we can represent the diffusional transport by

$$\frac{dm_t}{dt} = (m_t^e - m_t)\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{7}$$

Using Eqs. (2), (3) and (7) to obtain

$$\frac{dC_t}{dt} = -\frac{Q}{V}C_t - \frac{W}{M_{oil}V}(m_t^e - m_t)\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{8}$$

Assume that at equilibrium, a linear relationship exists between the oil concentrations in the solution and in the solid phase

$$C_t^e = Km_t^e \tag{9}$$

where K is the isotherm constant which has the unit of mol/l.

The total mass balance equation for oil also holds for equilibrium values, thus

$$M_t = m_t^e W + M_{oil} C_t^e V. \tag{10}$$

Eqs. (7)–(10) can be solved simultaneously to obtain the dynamic response of the oil concentration histories in the surfactant solution and in the solid waste during the washing process. C_t could be to design a treatment method which would permit the reuse of the surfactant and water. However, in this paper, we will only discuss the analysis of m_t, because this is the key process variable which describes the cleanness of the solid matrix.

Although a mass transfer model has been developed, the value of the overall mass transfer coefficient λ is still an unknown. The approach which is used to estimate λ is described in Section 4.2.

4.2. Estimation of the mass transfer coefficient

The lumped parameter approach is sometimes convenient for analyzing remediation process that involves irregular particulate solids. For instance, it has been used to estimate the mass transfer coefficient in the process of soil clean up by aeration [10]. This microscopic approach lumps the internal geometric factors of the particles and thus, simplifies the oil mobilization mechanism by neglecting the solid surface details. Fig. 3 is a schematic of this approach. The batch waste is hypothetically partitioned into an array of volume elements. The mass transfer of oil from the waste particles to the moving surfactant solution is assumed to take place by diffusion from the interiors of the particles to the surface and then solubilization into the surfactant micelles. The inverse time constant for diffusion of oil from the interior of one element of this array is calculated by approximating the element as spherical, for instance, and then calculating

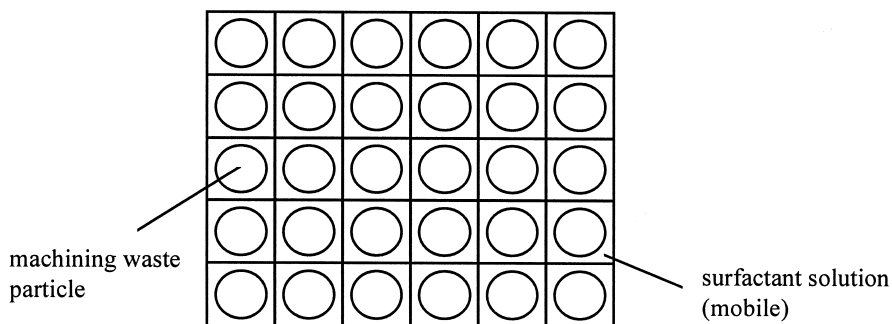machining waste particle

surfactant solution (mobile)

Fig. 3. Schematic of the lumped parameter approach.

the lowest non-zero eigenvalue for the appropriate diffusion problem [10]. If we assume spherical symmetry, the appropriate diffusion equation is:

$$\frac{\partial m}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial m}{\partial r} \right) \tag{11}$$

where D (m^2/s) is the effective diffusion coefficient which characterizes the internal diffusion of oil, and $m(r,t)$ (g oil/g waste) is the oil concentration at a distance r from the center of the element at time t.

Clean surfactant solution, which is charged into the tank from the bottom, continuously flows through the waste elements and flows away with solubilized or dissolved oil. It is reasonable to assume the washing solution that contacts the waste bed is practically oil-free [11], thus, the boundary conditions for a sphere of radius R are:

$$m(0,t) = \text{finite}$$

$$m(R,t) = 0$$

The initial condition for the oil diffusion is:

$$m(r,0) = m_0.$$

Using the method of separation of variables and the initial and boundary conditions, the diffusion equation can be solved and the value of the inverse time constants can be calculated [12]. With one boundary condition, we first obtain

$$m(r,t) = \sum_{n=1}^{\infty} C_n r^{-1} \sin\left(\sqrt{\frac{\lambda_n}{D}} \, r \right) \exp(-\lambda_n t) \tag{12}$$

The constant term C_n is obtained by using the initial condition

$$C_n = \frac{2 m_0 R}{\pi} \frac{(-1)^{n+1}}{n} \tag{13}$$

Therefore,

$$m(r,t) = \frac{2 m_0 R}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} r^{-1} \sin\left(\sqrt{\frac{\lambda_n}{D}} \, r \right) \exp(-\lambda_n t) \tag{14}$$

Applying the second boundary condition to Eq. (14) yields

$$\sin\left(\sqrt{\frac{\lambda_n}{D}} \, R \right) = 0 \tag{15a}$$

which means

$$\lambda_n = \left(\frac{n\pi}{R} \right)^2 D \quad n = 1,2,3\ldots \tag{16a}$$

We can see that the value of λ_n is determined by the oil diffusion coefficient and the size of the waste particles. The lowest non-zero eigenvalue λ_1 is:

$$\lambda_1 = \left(\frac{\pi}{R}\right)^2 D \tag{15b}$$

which is the first inverse time constant in the summation for $m(r, t)$.

This lumped parameter approach is based on one microscopic diffusion equation inside the waste particles. The vigorous solution of this equation provides the values for λ_n, $n = 1, 2, \ldots$, the inverse time constants for diffusion. Because of the lack of information about λ, the overall mass transfer coefficient inside the particles, it is reasonable to use one of the inverse time constants as an estimate for λ. The lowest non-zero eigenvalue λ_1 can be used to simulate conservatively the oil decay rate due to the diffusional transport of oil from the interiors of the waste particles to the surface where the spatial concentration gradient inside the particles can be neglected (i.e. time is the only independent variable) [2,5,10].

4.3. Modeling results

The parameters used in the mass transfer model are listed in Table 2. The diffusion coefficient of the oil in surfactant solution is obtained from the available literature [2]. The value of K is obtained in small scale batch washings. The value of the overall mass transfer coefficient is calculated by using Eqs. (15a) and (15b). The other parameters are chosen to be consistent with the typical surfactant washing process. The effective diameter of the particles will be varied to examine its influence on the washing efficiency. We choose not to study the influence of the surfactant solution flow rate because in a diffusion limited process, only marginal improvement in oil removal can be gained by using more solution. Simply increasing the solution flow rate is neither an economical nor a practical way to improve the cleaning efficiency.

The theoretical curves are plotted from the data obtained by solving the model equations numerically for a 60 min washing process. Fig. 4 shows the influence of the waste particle size on oil removal efficiency. Since the value of λ_1 is inversely proportional to the square of waste clump size, one can expect a strong increase of the cleaning efficiency as the particle size decreases. When the effective radius of the particle is reduced from 1.5×10^{-3} to 1.0×10^{-3} m, the residual oil content in the waste is reduced by approximately 40%. If the particle size is further reduced to

Table 2
Model parameters for semi-continuous surfactant washing

|	
Linear isotherm constant, K	0.0960 l/mol
Initial oil concentration in machining waste, $m(t = 0)$	0.2123 g oil/g waste
Effective diffusion coefficient of oil, D	10^{-10} m^2/s
Effective radius of machining waste particles, R	0.5×10^{-3}, $(1.0 \times 10^{-3}, 1.5 \times 10^{-3})$ m
Inverse time constant for diffusion, λ_1	0.00394, $(9.86 \times 10^{-4}, 4.38 \times 10^{-4})$ s^{-1}
Amount of machining waste being washed, W	100 g
Volume of surfactant solution in the tank, V	3.0 l
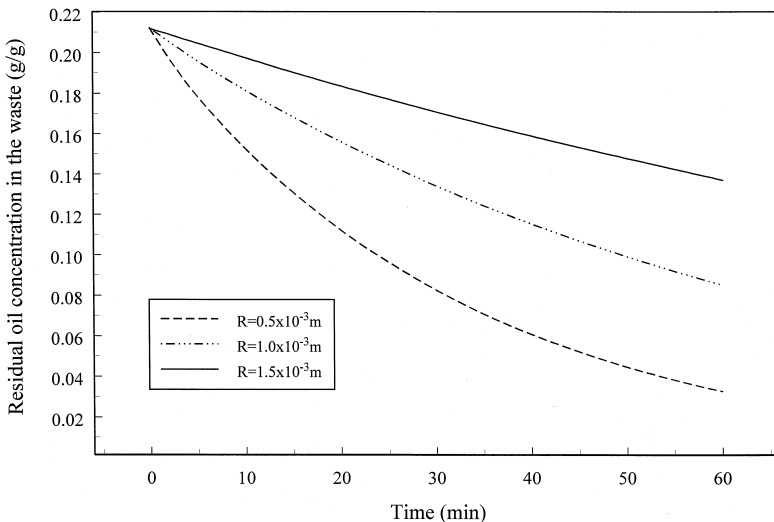
Fig. 4. Oil concentration history in machining waste for varying particle size (aqueous surfactant washing).

0.5×10^{-3} m, the oil content then is reduced by another 40%. Therefore, it can be concluded that a fine pre-washing pulverization is a very effective way to increase oil removal efficiency without increasing any other operation cost.

5. Mechanisms of SCCO$_2$ cleaning

The advantage of using SCCO$_2$ as solvent is that its density, and hence, solvent effectiveness, can be controlled by pressure and temperature. Also, its liquid-like density and gas-like viscosity, coupled with diffusion coefficient that is at least an order of magnitude higher than those of liquids, contribute to enhancement of mass transfer [13]. In addition, the non-toxic, non-flammable nature of CO$_2$ and its low critical temperature and pressure ($T_c = 31.1°C$, $P_c = 78.0$ atm) also make it a preferred solvent. In the SCCO$_2$ cleaning process, the recovery of solvent and the isolation of extract can be accomplished by a simple mechanical pressure reduction, and there is no waste water produced nor expensive surfactants required. Among the disadvantages of this technique are higher-pressure operation and the difficulty of handling very fine solids in a supercritical extractor.

The mechanism of SCCO$_2$ cleaning is driven primarily by the solubility of the oil, which is extracted from the solid and dissolved directly into the mobile phase due to the increased solvating power of CO$_2$ at the temperature and pressure above its critical point. The low viscosity of the mobile phase facilitates the penetration of CO$_2$ into the solid particles and the rapid diffusion of CO$_2$ with dissolved oil back to the bulk phase. Additionally, CO$_2$ will dissolve in the oil to some extent, reducing the viscosity of the oil and its surface tension, which also facilitates the oil removal. Because of the

relatively low solubility of oil in CO_2, the weak interaction between the solute and solvent, and the weak interaction of CO_2 with the solid surface (i.e. no preferential wetting), the strength of the adsorption between the oil and the solid phase may become a limiting factor, in which case the extraction rate will be primarily controlled by the kinetics of the desorption step. Dahmen et al. [14] used $SCCO_2$ extraction to clean a metal cutting waste contaminated with oil. They studied the influence of solvent flow rates on the extraction efficiency and found that within the experimental error, no significant influence could be detected, which means that this extraction process was primarily controlled by the desorption kinetics.

6. Experimental procedure

The apparatus used in $SCCO_2$ cleaning is shown in Fig. 5. The main components were an ISCO 260D syringe pump, ISCO SFX 2–10 supercritical fluid extractor, ISCO series D pump controller, a restrictor, a temperature controller for the restrictor, and a cold trap.

The untreated machining waste was placed in the extraction cell and extracted by pure $SCCO_2$ for a total of 60 min. The temperature and pressure chosen for the experiments (80°C, 340 atm) are consistent with the US Environmental Protection Agency Method 3560 (EPA 3560) which is used for Total Petroleum Hydrocarbon analysis [15]. The extraction data are shown in Fig. 6. Every 10 min, the extraction is stopped and the cell was weighed to obtain the oil concentration change with time during the process. A gravimetric method is developed to determine the oil concentration in the solid sample. The weight of an extraction cell consisted of the weight of three elements: the empty cell, the inert solid components in the machining waste, and the oil. Because only oil dissolves in $SCCO_2$, the weight loss during the extraction is due only to the oil removal. After the extraction is completed, some samples were sent to Galbraith for analysis and the analytical results were used to compare with those obtained by the gravimetric calculation. It reveals that the lab results consistently show
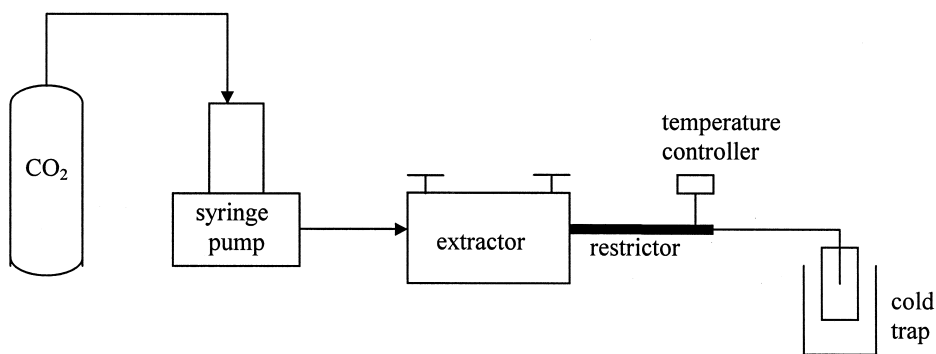

Fig. 5. Schematic of the semi-continuous $SCCO_2$ extraction apparatus.
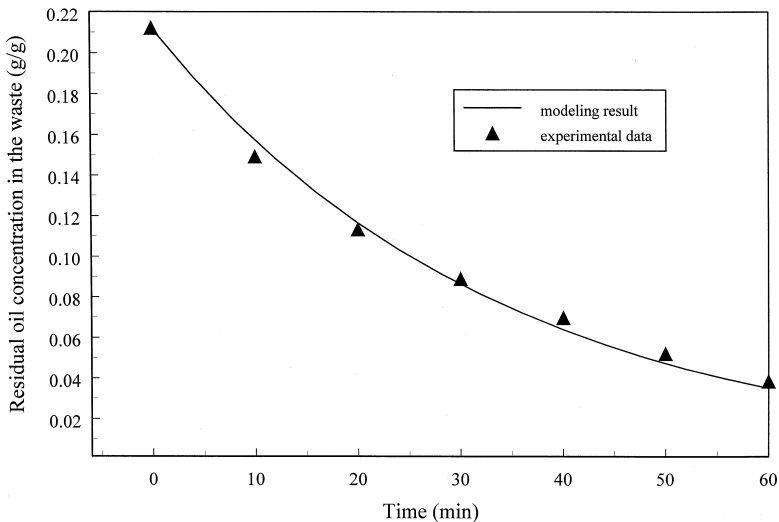
Fig. 6. Oil concentration history in machining waste ($SCCO_2$ extraction).

more oil removal with a difference of approximately 10%, which may be caused by the oil loss due to evaporation during sample handling, shipping and transportation.

To decide whether the different solvent flow rates have any significant influence on oil removal, the flow rate of CO_2 was increased from 0.2 to 0.6 ml/s. It was found that at the end of the extraction, the oil removal was only increased by 3%. Therefore, in our experiments, the cleaning efficiency was assumed to be independent of solvent flow rate. The syringe pump was set to keep the system pressure constant instead of a constant solvent flow rate.

7. Mathematical modeling for $SCCO_2$ cleaning

$SCCO_2$ extraction has been extensively studied for its application in the regeneration of contaminated activated carbon. The extraction of ethyl acetate from contaminated carbon has been investigated by many researchers. Tan and Liou [16] considered desorption of ethyl acetate as an irreversible desorption process. But Recasens et al. [17] obtained better results by describing desorption as an equilibrium process. In the work of Srinivasan and McCoy [18], the solid bed was considered a well-mixed reactor, with first-order reversible adsorption of the solute. In modeling $SCCO_2$ extraction of PAH from the contaminated soil, Kothandaraman et al. [19] used a simple, single-parameter model with linear desorption kinetics to fit the desorption data. It should be noted that there are many possible extraction models which could be derived, depending on the amount of detail required for accuracy and the number of parameters which can be estimated. In our work, we assume that the dissolved oil molecules will stay in the mobile phase, hence, the desorption of oil from the solid waste will be described by an irreversible desorption equation.

The extraction is conducted using a fixed bed of spherical particles of the machining waste, with an initial concentration of adsorbed solute (oil) q_0. The solid bed is viewed as well-mixed with efficient contacting by CO_2. For this paper, mass transfer resistance is considered to be negligible. Assume that the frictional pressure drop through the bed is negligible so that the linear velocity through the bed can be considered constant. Pure solvent enters the bed at a constant interstitial velocity and the flow pattern is described by plug flow. The void volume is initially free of solute, and the extraction process is isothermal. Based on the above assumptions, the mass balance in the bulk phase in the extraction cell may be written as:

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial z} + \frac{1 - \varepsilon}{\varepsilon}\rho\frac{\partial q}{\partial t} = 0 \tag{16b}$$

where C (g oil/ml of fluid) is the oil concentration in the mobile fluid phase, q (g oil/g waste) is the oil concentration in the machining waste, ρ is the density of the machining waste (g/ml), v (cm/min) is the interstitial linear velocity of the solvent, z (cm) is the axial position in the solid bed, and ε is the void fraction of the bed.

Because of the low solubility of oil in CO_2 (approximately 10^{-2} g oil/ml of fluid), the change in solute concentration in the mobile phase is very small through the bed which allows one to ignore the variance in the concentration gradient in the axial direction and consequently, assume a constant gradient through the bed. Therefore, Eqs. (16a) and (16b) can be written as:

$$\frac{dC}{dt} + \frac{uC}{\varepsilon V_{bed}} + \frac{1 - \varepsilon}{\varepsilon}\rho\frac{dq}{dt} = 0 \tag{17}$$

where u (ml/min) is the interstitial volumetric flow rate of the solvent, and V_{bed} (ml) is the volume of the solid waste bed (including void volume).

Assume that the desorption of oil from the solid waste to the mobile phase can be considered as an irreversible process. Because of the lack of information on the effective diffusivity of oil in $SCCO_2$ phase and the adsorption isotherms, the mass balance in the solid bed is expressed in terms of linear desorption kinetics [16] which may be written as:

$$\frac{dq}{dt} = -k_d q \tag{18}$$

where k_d (min^{-1}) is the desorption rate constant. This model presumes that the solvent flow rate and consequently the residence time has no influence on oil desorption (i.e. oil concentration decay rate in the solid phase). The desorption profile is only a function of the k_d value.

Eqs. (17) and (18) define a one-parameter (k_d) irreversible desorption kinetic model. The initial condition is:

$$q = q_0 \quad \text{at } t = 0$$

From Eq. (18) and the initial condition, the desorption profile can be obtained:

$$q(t) = q_0 e^{-k_d t} \tag{19}$$

Substituting Eqs. (18) and (19) into Eq. (17) yields

$$\frac{dC}{dt} + \frac{uC}{\varepsilon V_{bed}} - \frac{1-\varepsilon}{\varepsilon} \rho k_d q_0 e^{-k_d t} = 0 \tag{20}$$

Since time is the only independent variable, this equation can be solved in the Laplace domain to obtain the effluent concentration history:

$$C(t) = \frac{\frac{1-\varepsilon}{\varepsilon} \rho q_0 k_d \left[\exp(-k_d t) - \exp\left(-\frac{t}{\varepsilon \tau}\right) \right]}{\frac{1}{\varepsilon \tau} - k_d} \tag{21}$$

where τ refers to a residence time, given as the ratio of the total volume of the bed to the flow rate of the mobile phase at the conditions of the bed. One should keep in mind that the oil concentration in the fluid phase will vary with different solvent flow rates, even though the amount of oil removed from the solid is not affected by the flow rate (i.e. the volume of solvent used). However, the fluid-phase oil concentration will not be addressed in this paper, as our interests are focused on the cleanness of the solid phase.

The parameters used in this model are summarized in Table 3. The value of the desorption rate constant k_d is determined by fitting the experimental data into the modeling equation and will vary within a reasonable range ($\leq 10\%$) to investigate its influence on oil removal efficiency.

Fig. 6 displays the oil concentration histories in the machining waste during a 60 min extraction and the modeling results are compared with the experimental data. With the calculated k_d, the two sets of extraction data match well under our operating conditions. Fig. 7 shows the oil concentration histories in the machining waste at different k_d values. These computed curves indicate that the effect of the desorption rate constant on oil removal is not prominent. The 10% increase or decrease of k_d value approximately results in a 15% difference in oil removal. This reminds us that although the irreversible desorption step is a limiting factor which primarily controls the cleaning efficiency, the desorption would be limited by the equilibrium distribution of oil between the adsorbent and $SCCO_2$ (i.e. the adsorption equilibrium) in the absence of mass transfer resistance.

In order to make a direct comparison between aqueous surfactant washing and $SCCO_2$ extraction, the results obtained from the mass transfer model and the linear

Table 3
Model parameters for semi-continuous $SCCO_2$ extraction

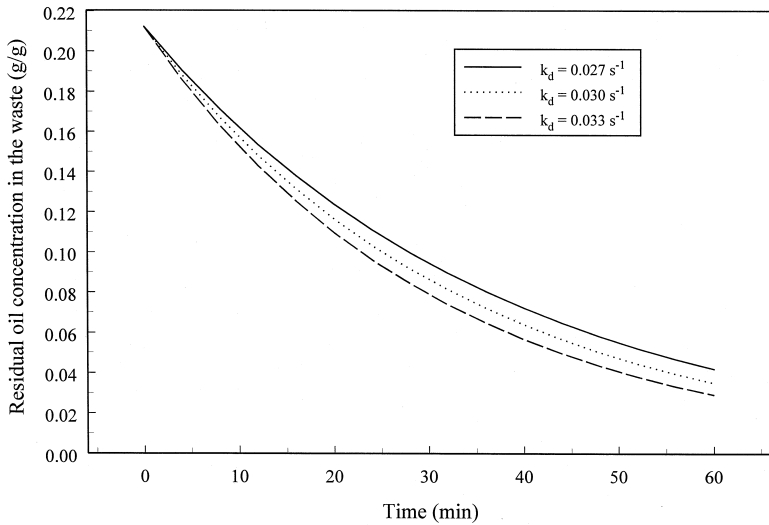|	
Desorption rate constant, k_d	0.030, (0.033, 0.027) min^{-1}
Initial oil concentration in the machining waste, q_0	0.2123 g/g waste
Density of the machining waste, ρ	2.6 g/ml
Volume of the solid bed, V_{bed}	8.0 ml
Void fraction of the solid bed, ε	0.3
Extraction time, t	60 min
Extraction temperature	80°C
Extraction pressure	340 atm

Fig. 7. Oil concentration history in machining waste for varying k_d value (SCCO$_2$ extraction).

desorption model are shown in Fig. 8. It can be seen that the cleaning efficiency of these two technologies is very close to each other. At the end of a 60 min process, the residual oil content is 0.0328 g/g and 0.0351 g/g for washing and extraction products, respectively. Although the technical comparison does not show a prominent difference between the performances of aqueous washing and SCCO$_2$ extraction, our own experi-
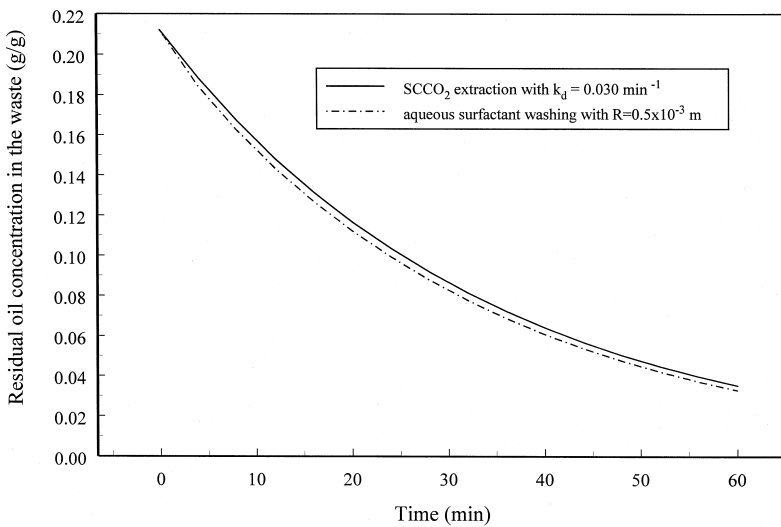

Fig. 8. Oil concentration history in machining waste (comparison between aqueous surfactant washing and SCCO$_2$ extraction).

ences tell us that the industry is more interested in applying aqueous surfactant washing to solve this solid waste problem, due to the maturity and the popularity of this technology. It should be noted that the economic aspects will play a critical role in a comprehensive evaluation of these two cleaning procedures, especially in larger scale applications. The price of the specialty surfactant package and the cost of waste water treatment will strongly affect the practicality of aqueous surfactant washing. On the other hand, the economics of the washing technology also depends on the success of the downstream processing which can permit the reuse of the expensive surfactant and thus result in huge savings in the investment. While evaluating $SCCO_2$ extraction, the cost of high-pressure equipment and huge energy consumption are considered as its disadvantages. These considerations are the focus of our current design efforts.

8. Conclusion

Two competitive cleaning technologies, aqueous surfactant washing and $SCCO_2$ extraction, were examined for their utility in removing oil from a machining waste. The aqueous washing process was described by a mass transfer model with the overall mass transfer coefficient estimated by a lumped parameter approach which neglected the details inside the particles. This model implied that the oil removal in a washing process was controlled primarily by the diffusional transport of oil from the interiors of the particles to the surface and consequently, was strongly affected by the particle size. A fine pre-cleaning pulverization could greatly reduce the diffusion resistances and improve cleaning efficiency without increasing any other operation cost. On the other hand, the oil removal efficiency in a diffusion limited process could be expected to have a weak dependence on the volumetric flow rate of the surfactant solution.

In $SCCO_2$ extraction, a batch of machining waste was treated as a well-mixed bed and the desorption of oil from the solid was described by an irreversible desorption kinetic equation which implied that the solvent flow rate had no influence on oil removal efficiency. This model was supported by the experimental data obtained under the extraction conditions of EPA 3560. The reasons for this desorption-dominating mechanism may be the low solubility of oil in the mobile phase, the weak bond between oil and CO_2 when compared to the bond between the adsorbed oil and the adsorbate, and the weak interaction of CO_2 with the solid surface.

Theoretical calculations showed that aqueous surfactant washing and $SCCO_2$ extraction have similar cleaning efficiencies. However, a more complete and accurate comparison between these two technologies is needed where the equipment cost (a determinant factor for $SCCO_2$ extraction) and the downstream processing cost (a determinant factor for aqueous surfactant washing) are also thoroughly analyzed.

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