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Journal of Hazardous Materials B131 (2006) 195–199

Journal of Hazardous Materials

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Treatment of oil-in-water emulsions: Performance of a sawdust bed filter

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Received 11 March 2005; received in revised form 13 September 2005; accepted 14 September 2005
Available online 2 November 2005

Abstract

The effect of operating conditions on the performance of a sawdust bed filter used for the treatment of an oil-in-water emulsion was investigated. A metalworking fluid (3 vol.% oil) was used as oil-in-water emulsion and sawdust as filter medium and sorbent. Because of the high stability of the emulsion, small amounts of inorganic salt (calcium sulphate) were mixed with the sorbent, acting as coagulant to achieve the emulsion breakdown. The influence of flow rate, bed height, temperature and the amount of coagulant salt added was studied. Experimental results show that several processes are involved in oil removal from oil-in-water emulsions, i.e. coagulation, coalescence, adsorption or straining. More than 99% of oil content in the influent stream was removed. Experimental results show that low-cost sorbents like sawdust are feasible to be used in the treatment of oil-in-water emulsions if small amounts of coagulant salts are added to the filter media.

Keywords: Deep bed filtration; Oil removal; Waste emulsion; Sawdust; Coagulant salt

1. Introduction

The current treatment methods of waste emulsified oils before their disposal remain unsatisfactory. Emulsifiable or water-miscible cutting oils are used in metalworking industries as lubricants and coolants yielding better surface finishes and protecting tools from abrasive wear. Cutting oils consist of a suspension of oil droplets in water, stabilised by surfactants, and usually contain several compounds, such as biocides, defoamers, rust inhibitors, extreme pressure additives, etc. Once the emulsions lose their functional properties, they must be treated before their disposal because of the toxic and hazardous properties of their components. Even very low oil concentrations are toxic for microorganisms responsible for biodegradation in conventional sewage processes, and therefore removal of the oil phase is essential before effluent disposal. The oil removal process involves usually emulsion destabilisation, which is not an easy stage, because of the emulsifying agents used in their preparation.

For the removal of the oil phase, which has a high organic matter content (50,000–80,000 mg/L COD), several techniques have been proposed [1] and, among them, deep bed filtration has been reported as an efficient process [2–4]. However, the feasibility of fixed beds depends to a large extent on the costs of the filter media and, therefore, research has been focused on the use of solid waste materials or cheap and abundant natural products.

Sawdust is an easily available by-product in timber and paper industry and exhibits good sorbent characteristics for the treatment of wastewater containing heavy metals [5–12], dyes [13–19], or phenolic compounds [20,21]. In many cases, a chemical pretreatment of sawdust is needed to activate the sorption sites [12,14,22].

The aim of this work is to assess the performance of sawdust as filter media for the treatment of oil-in-water emulsions, and to study the influence of the operating conditions. A cutting oil, used in metalworking operations, was selected as oily waste.

2. Materials and methods

Oil-in-water emulsions were prepared by mixing a commercial cutting oil Licena (CEPSA Co., Spain) in deionised water. All experiments were carried out with emulsions containing 3 vol.% of oil. The influent oil concentration was kept constant at about 24,000 mg/L.

Eucalyptus sawdust was provided as powder by a paper mill company (ENCE, Navia, Spain) and was used without previous

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doi:10.1016/j.jhazmat.2005.09.023

Table 1
Characteristics of the eucalyptus sawdust

Characteristic	Value
Density (kg/dm^3)	0.782
Porosity (%)	66.5
Mean average diameter (μm)	131.6
10% percentile (P_{10}, μm)	10.4
60% percentile (P_{60}, μm)	113.7
Coefficient of non-uniformity (P_{60}/P_{10})	10.9

treatment. The main characteristics of the sawdust are summarised in Table 1. These data were obtained using a Mastersizer S long bench apparatus (Malvern Instruments Ltd.).

In order to promote coagulation of the oil droplets by surface charge neutralisation, calcium sulphate ($CaSO_4 \cdot 2H_2O$, Panreac, PA) was mixed with the sawdust. Preliminary tests showed that calcium ions helped to neutralise the negative zeta potential of oil droplets, overcoming the electrostatic repulsion and enhancing droplets to coalesce. The choice of the calcium sulphate was based on its low solubility (0.20 g $CaSO_4 \cdot 2H_2O$/100 g of water) with respect to another calcium salts of higher solubility, in order to ensure the presence of the calcium cations in the bed for longer times. The bed filters were divided in two sections of variable height: an upper salt/sawdust mixed bed and a lower sawdust bed. The purpose of the splitting was to promote coalescence in the first section and oil removal in the second one.

Deep bed filtration experiments were conducted using a Pharmacia Biotech column model XK26/20, 0.2 m long. The inner glass tube was replaced by a 26 mm diameter methacrylate column. An external circulating bath allowed to carry out the experiments at the desired temperature. Filter bed heights ranged from 30 to 55 mm. The pressure drop across the filter bed was measured with a piezoelectric transducer DS Europe, model LP634, 1–10 bar. A schematic diagram of the experimental set-up is shown in Fig. 1.

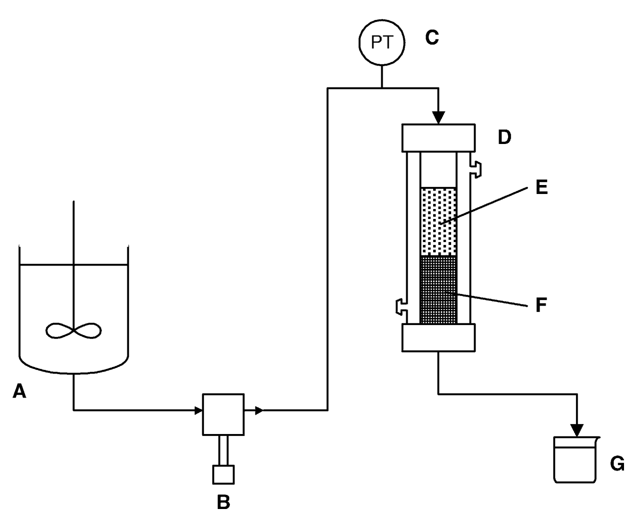

Fig. 1. Experimental set-up. A: Stirred reservoir (feed); B: piston pump; C: pressure transducer; D: column; E: mixed salt/sawdust bed; F: single sawdust bed; G: beaker (treated effluent).

Experiments were carried out by pumping the oil/water emulsion from a 2 L container through the filter bed by a Dosapro Milton Roy piston pump, that allowed to monitor the flow rates. The oil concentration was measured as a function of time and experiments were ended when effluent breakthrough took place, due to oil saturation of the bed, or when the pressure at the inlet rose up to 6 bar.

Pressure drops across the bed, oil content and COD values in the effluent were measured varying the operating conditions: flow rates, amount of coagulant salt added, bed height and temperature.

Oil concentrations were determined by IR spectroscopy, using a Horiba OCMA 310 oil content analyser. The COD analyses were carried out by the reactor digestion method [23] using a Hach DR/2010 UV spectrophotometer. A Crison conductivimeter micro CM2202 was also used to monitor the conductivity in the feed and outlet streams.

3. Results and discussion

3.1. Effect of the amount of coagulant salt

Data for the ratio of oil concentration at the outlet of the filtration bed and concentration of the inlet stream (C/C_0) as a function of the volume treated, for beds with varying amounts of coagulant salt are shown in Fig. 2. The chemical oxygen demand (COD) at the outlet follows a pattern similar to oil concentration. If there is no oil content in the effluent, a reduction of COD higher than 95% is achieved. It is observed that the addition of calcium sulphate is essential to achieve oil removal and larger volumes could be treated when higher amounts of salt were added. The dissolved salt ions compress the electric double layer around droplets, neutralise repulsive forces among them and between droplets and sawdust particles and, hence, enhance coalescence of oil droplets. Moreover, the lack of electrostatic repulsion improves the physical adsorption of the oil droplets on the sawdust surface, originally negative-charged. Thereby, the oil droplet size is increased and its charge neutralised, so that the disperse phase can be retained in the filter media interstices. Furthermore, some authors have pointed out that calcium salts activate the sorption sites of sorbent materials in the removal of different unwanted materials from water [12,22]. In this work, sawdust was not pretreated to activate its sorption capacity and

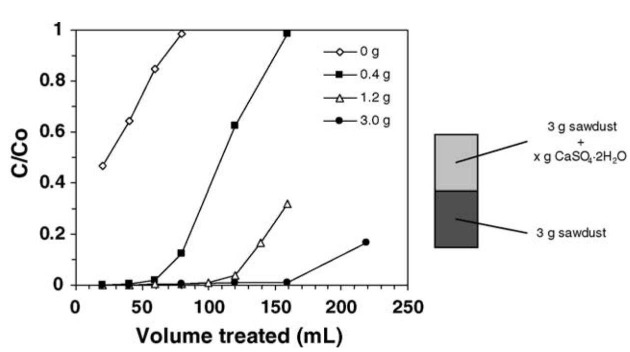

Fig. 2. Effect of the amount of coagulant salt. Sawdust bed = 6 g; bed height = 36 mm; flow = 20 mL/h; C_0 = 24,000 mg/L oil.

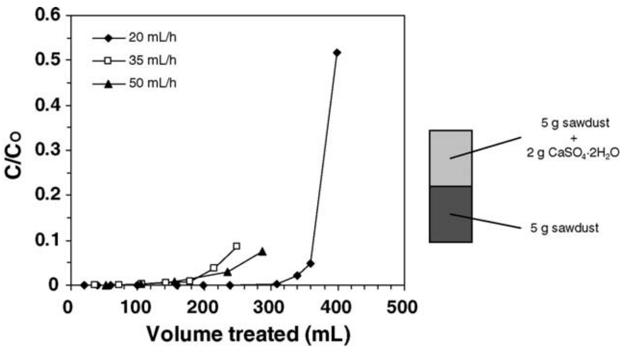

Fig. 3. Effect of flow rate. Sawdust bed = 10 g; bed height = 58 mm; $CaSO_4 \cdot 2H_2O$ = 2 g; C_0 = 24,000 mg/L oil.

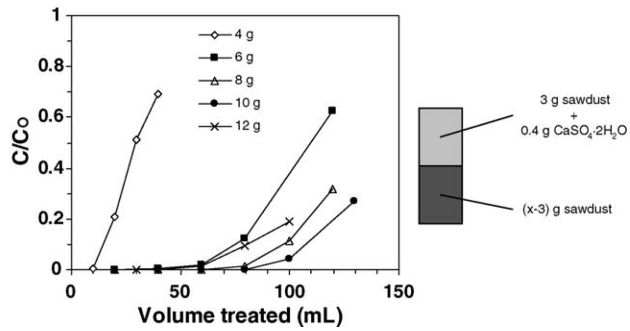

Fig. 4. Effect of sawdust bed mass. $CaSO_4 \cdot 2H_2O$ = 0.4 g; C_0 = 24,000 mg/L oil; flow = 20 mL/h.

likely, adding the coagulant salt, coalescence and straining phenomena prevail over the ion-exchange and adsorption processes. Because of its low solubility in water compared to another calcium salts, i.e. $CaCl_2$, calcium sulphate is not entrained to an appreciable extent by the effluent, allowing to remove larger amounts of oil when the amount of salt is increased. Conductivity measurements in the outlet stream were carried out to monitor the entrainment of the inorganic salt by the effluent. Results showed a constant use of the calcium sulphate, with values depending on the salt concentration but always lower than 800 μS/cm, far below the conductivity of a saturated solution of calcium sulphate (ca. 1500 μS/cm), preventing the possibility of salt precipitation.

3.2. *Effect of the flow rate*

As it is shown in Fig. 3, the filter media performs better at low flow rates. This might be explained because the oil droplets coalesce to a droplet size large enough to be entrapped, as a result of longer residence times in the bed. Also, at a certain flow rate, the void spaces are progressively clogged by the retained oil, and hence the local velocity of the liquid phase increases, weakening the interaction forces and driving the disperse phase droplets more deeply into the bed. This entrainment ensures a better use of the filter bed layers and filtration runs take longer time. However, a flow rate is reached above which the sawdust bed is not able to retain the oil present in the feed and it goes through with the outlet effluent. Moreover, the head loss across the granular media itself is a linear function of velocity, regardless of the degree of clogging, supporting the suitability of low flow rates, when it is possible. Finally, it is worth to notice that liquid–liquid phase separations are more sensitive than the corresponding liquid–solid to the influence of flow rate, because of the fact of droplet deformation.

3.3. *Effect of the bed height*

To study the influence of bed height on oil removal the amount of sawdust was increased, keeping constant the amount of coagulant salt. As shown in Fig. 4, an increase in the bed height, which is directly related to bed mass, allows to treat a larger volume of emulsion, until a critical bed height value is reached. Above this critical height the pressure drop across the bed increases exponentially with time, while for shorter beds, the pressure drop remains constant or increases linearly (Fig. 5). The exponential increase in pressure drop suggests the occurrence of surface straining or clogging in a deep layer of the bed. As the bed height is increased, higher inlet pressures are needed to maintain a certain flow rate of the feed emulsion. Hence, the bed porosity is reduced, the void spaces become smaller and the velocity is increased. An increased velocity increases the drag forces between the liquid and the granular media. Moreover, in this set of experiments, the amount of calcium sulphate mixed with the sawdust was relatively low (0.4 g $CaSO_4 \cdot 2H_2O$). In conclusion, the oil droplets are not easily retained but driven deeper into the bed, coalescing and reaching a size large enough to cause clogging of an inner layer. At that moment, the linear increase of pressure with time shifts suddenly to an exponential increase and the filtration must be discontinued.

3.4. *Effect of temperature*

Two sets of experiments, using different amounts of coagulant salt, were carried out to study the effect of temperature on the bed performance. Slight changes in oil removal were found, although the best performance seemed to be achieved at the

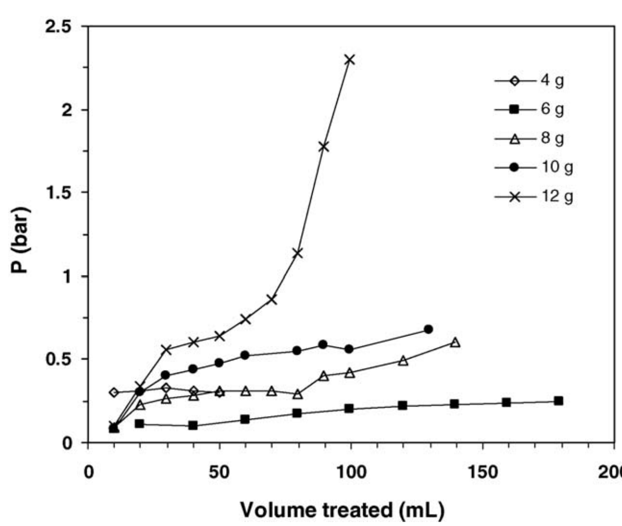

Fig. 5. Effect of bed mass on the head loss across the sawdust bed. $CaSO_4 \cdot 2H_2O$ = 0.4 g; C_0 = 24,000 mg/L oil; flow = 20 mL/h.

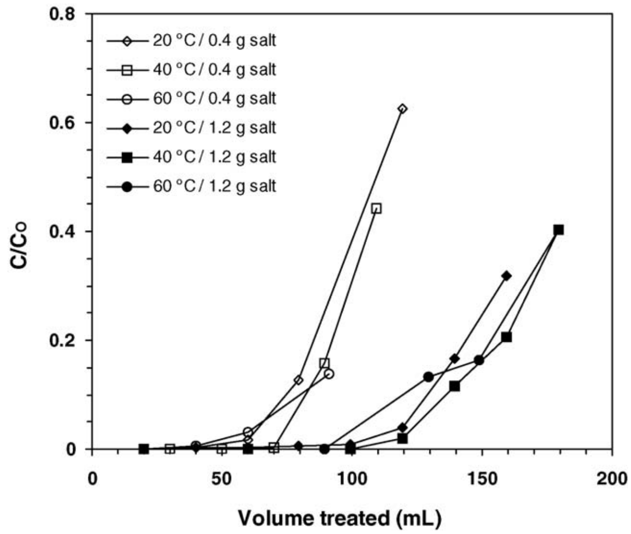

Fig. 6. Effect of temperature. C_0 = 24,000 mg/L oil; flow = 20 mL/h; sawdust bed = 6 g.

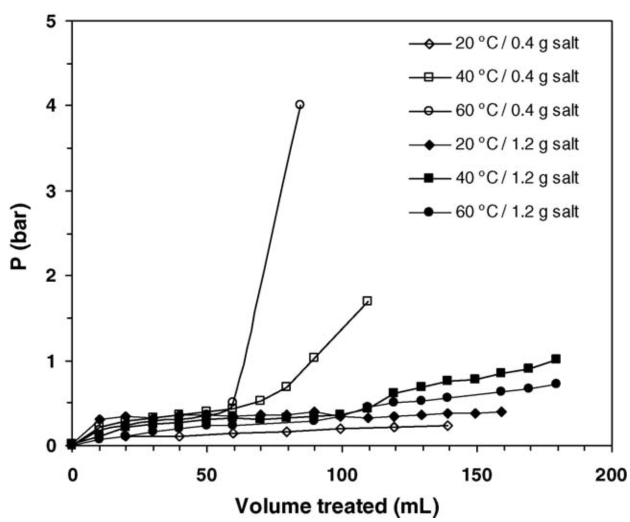

Fig. 7. Effect of temperature on the head loss across the sawdust bed. C_0 = 24,000 mg/L oil; flow = 20 mL/h; sawdust bed = 6 g.

intermediate temperature (40 °C), as shown in Fig. 6. However, the pressure drop across the filter had a different behaviour, as shown in Fig. 7. An exponential increase in pressure drop was observed at high temperatures and for small contents of calcium sulphate. High temperatures usually enhance coalescence, due to the lower fluid viscosity and the rise in the number of collisions between droplets, since their mobility is increased. But, likewise, the probability for a droplet to be entrapped is reduced. An increase in temperature also leads to a less favourable adsorption equilibrium. The lack of coagulant salt and high temperatures increases the oil droplet residence time in the bed, and hence coalescence and layer clogging are also favoured.

4. Conclusions

Experiments on oil removal by deep bed filtration under varying conditions of temperature, flow rate, bed height or amount of coagulant salt added show that several processes, e.g. coagulation, coalescence, adsorption and straining are involved. Moreover, operating conditions determine the controlling mechanisms, being most desirable those conditions that entail a gradual aggregation and retention in the filter media.

Oil removal ratios greater than 99% were reached, keeping the pressure drop across the bed far below 0.5 bar in the best operating conditions. Furthermore, the decrease in COD was higher than 95% and, therefore, the processed effluent might be treated in a conventional wastewater treatment plant.

The easy availability of sawdust and calcium sulphate makes of this process a suitable technique for waste cutting oils treatment and removal. A further study would be necessary to determine if the spent sawdust filter bed, once it becomes saturated with oil, might be used as fuel in power plants.

Acknowledgements

Financial support by the Ministerio de Ciencia y Tecnología (MCYT, Spain) and the European Commission by means of projects 1FD97-0870 and PPQ2001-3442-C02-01 (European Regional Development Fund) is gratefully acknowledged.

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