Removal of exhausted oils by adsorption on mixed Ca and Mg oxides

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Abstract

Adsorption tests were performed on two different exhausted oils to reduce their polluting and health hazard potential: a "water-insoluble oil", utilised for automotive engine lubrication, and an "emulsified" oil, used as coolant for metal-cutting tools. Dolomite, a low-cost recovery material, was used to prepare two effective adsorbents: (a) a mixed Ca and Mg oxide obtained by thermal decomposition of dolomite at 1800°C, and (b) an activated material obtained by submitting this product to chemical treatment with HCl. Preliminary tests carried out with an excess of the former material showed that the insoluble oil was adsorbed with lower yield ($Y = 0.40$) than the soluble (emulsified) oil ($Y = 0.60$). The material activation with HCl remarkably improved the adsorption of soluble oil organic fraction ($Y > 0.90$), while only a little increase in the removal yield was observed for the insoluble oil ($Y = 0.44$). The results presented and discussed in this work pointed out that the products of dolomite calcination can successfully replace the conventional adsorbing materials in the removal of organic pollutants, with particular concern to exhausted soluble oils, which cannot usually be recycled, thus reducing the operational costs of their treatment. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The exhausted oils from industrial activities or operational maintenance of machines are usually disposed of by specialised firms, while the disposal of waste containing oils at low concentration occurs in conventional sewage treatment systems, causing environmental damages, in particular to the micro-flora responsible for the biological processes. So, to reduce the polluting power of oily wastes, they might be treated separately before discharge.

The removal of oils at low concentration presents some difficulties, because the usual systems cannot offer suitable solutions. The methods used more commonly are the sand filtration coupled to coagulation with $FeCl_3$ or polyaluminium chloride [1] or the adsorption on foamed polypropylene [2]. Granular charcoal was also used [3–5] because of its well-known adsorption capacity and the simplicity of its regeneration by heat treatment. Benito et al. [6] removed 75% of the emulsified oils contained in aqueous effluents by an integrated process of coagulation/flocculation followed by ultrafiltration, while Kong and Li [7] obtained 77% removal by permeation with a microporous hydrophobic membrane. However, the treatment of wastewater containing oily pollutants by the above methods is too expensive because of the high costs of both the adsorption materials and the operational systems.

For this reason, alternative organic and inorganic waste materials, among which bark [8], lignin [9],

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biomass [10], zeolite [11] and bentonite [12], were tested with success as adsorbents but mainly for the removal of metals.

On the other hand, there is a relative lack of information in the literature about the removal of organic pollutants by adsorption on waste or low-cost materials, such as fly ash [13], peat, steel plant slag, bentonite [14], soil organic matter [15], and alumina materials [16]. Even less is known about the use of these materials for oil removal [17].

This work aims at evaluating the possibility of removing both emulsified and insoluble oils using as adsorbents the products of thermal decomposition (mixed Ca and Mg oxides) of dolomite, that is a low-cost inorganic recycling material, mainly from the productions of refractory and replenishing materials for filtration. In order to increase the adsorption capacity of this material, it was also submitted to a chemical treatment with HCl.

2. Materials and methods

Two different materials were tested as adsorbents in this work for the removal of polluting oils: a mixed Ca and Mg oxide, obtained by decomposing dolomite at 1800°C according to the reaction:

$$MgCa(CO_3)_2 \rightarrow MgOCaO + 2CO_2 \qquad (1)$$
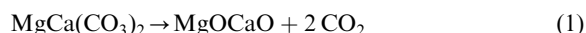
and the same material activated with a 37% (1:1 w/v) HCl solution at room temperature.

The average physical characteristics of both materials (specific surface area, total pore volume and pore diameter), determined by liquid nitrogen absorption using a Macropore Analyser (Unit 120, Carlo Erba, Milan), are summarised in Table 1 and compared with those of the starting raw dolomite. These results show that the thermal decomposition led to remarkable increase in total porosity (104%), pore diameter (113%) and specific surface area (119%), which were likely responsible for the improved adsorption properties of $MgO \cdot CaO$ with respect to the original dolomite. In addition, the successive treatment with HCl provoked a further 6% increase in pore diameter but appreciable decreases in both specific surface area (36%) and total porosity (39%).

These variations in the morphologies of both raw dolomite and mixed Ca and Mg oxide were confirmed by examination with a scanning electron microscope (ISI-SS-40), at a magnification of 5000, on samples previously covered by a thin layer (20 nm) of gold.

Two different exhausted oils were selected in this study, according to their affinity with water: a water-insoluble lubricating oil and a water-soluble (emulsified) oil. The former oil has some characteristics which suggest and justify its use as an alternative and/or integrative fuel, such as less sulphur content than fuel oil and comparable high heat value, even if it is characterised by higher metal content. On the other hand, the water-soluble oil used in this study was a commercial emulsion of insoluble oil in water obtained with emulsifying agents.

In each set of tests, carried out by using an oil/water (O/W) ratio increasing from 0.02 to 0.08, either oil was treated with both adsorbents, in order to select the most suitable adsorption conditions. For this purpose, 25 ml of waste samples were mixed for 10 min in a Jar-test apparatus at 140 rpm with a given amount (10 g) of adsorbent. Longer contact times did not show any significant improvement of the adsorption yield.

At the end of each test, 2 ml of 0.25% coalescent solution (Praestol, Cyanamid 444/K) were added to make the separation of phases easier. After waiting for a settling period of 30 min, 20 ml of supernatant were withdrawn, filtered trough Millipore filters with 0.45 μm pore diameter and submitted to COD analyses [18] to determine the amount of organic substances removed.

3. Results and discussion

The COD removal yield obtained by treating both soluble and insoluble oils with mixed Ca and Mg oxide is plotted against O/W ratio in Fig. 1. For the soluble (emulsified) oil, the removal yield reached a maximum value (0.60) at the lowest O/W ratio tested (0.02) and decreased progressively with an increase in this ratio. At the end of each adsorption test, the treatment with coalescent allowed to separate two phases: at the beginning, a thin oil layer appeared onto the surface of a turbid water phase, which was indicative of an

Table 1
Average physical characteristics of dolomite-derived adsorbents

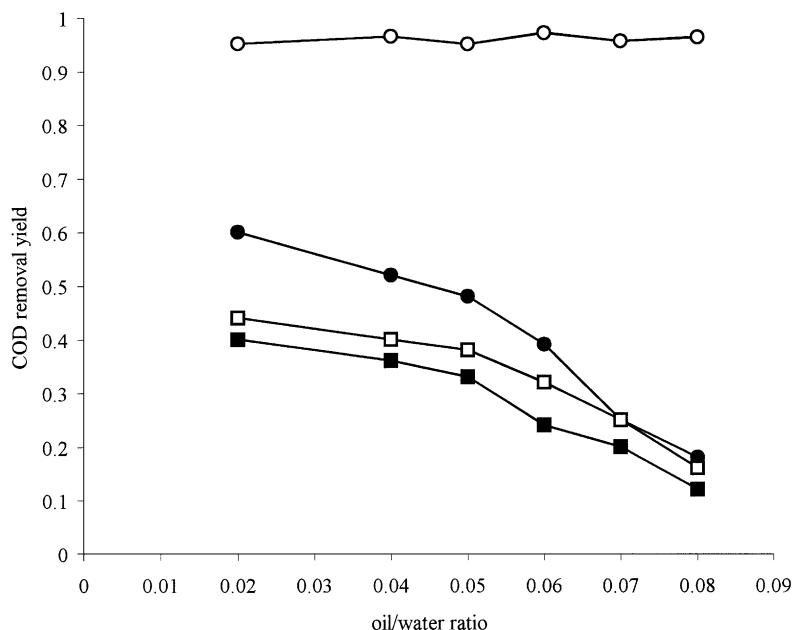| Characteristic	Raw dolomite	MgO · CaO	MgO · CaO activated with HCl
Specific surface area (m²/g)	8.34	18.27	11.70
Pore diameter (μm)	2.114	4.510	4.630
Total porosity (%)	21.50	43.97	26.60

Fig. 1. COD removal yields obtained for the treatment of (●) soluble and (■) insoluble oils with MgO·CaO and of (○) soluble and (□) insoluble oils with MgO·CaO activated with HCl.

incomplete separation. Several hours were necessary for obtaining a satisfactory separation.

The same qualitative behaviour of the COD removal yield was observed for the insoluble oil, but its maximum value (0.40) obtained at the minimum O/W ratio (0.02) was quite lower than that obtained with the emulsified oil. After treatment with coalescent, a thick oil layer formed onto the surface of the mixture, but no improvement of phases separation was achieved even after some days of settling time.

The micrographs of Figs. 2 and 3, which illustrate the morphologies of dolomite and MgO·CaO, respectively, show that the thermal treatment remarkably modified the material surface, namely increasing the specific surface area. This observation is confirmed by the experimental data of Table 1, which demonstrate that the thermal treatment at $1800°C$ is responsible for an increase in the specific surface area from 8.34 to $18.27 \, m^2/g$, a value which compares to those of well-known adsorbents [19]. The decomposition of calcium and magnesium carbonates into their respective oxides justifies the improvement of the adsorption capacity of mixed Ca and Mg oxide if compared with starting dolomite. For this reason, only the former material was used in the following adsorption tests either as such or activated with HCl.

The thermal and acid treatments of adsorption materials were studied by Pradas et al. [20], who demonstrated that the acid treatment decreased the
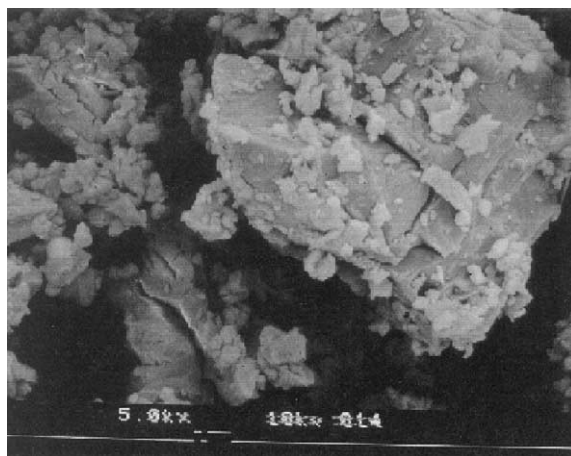

Fig. 2. Micrograph of a dry sample of dolomite. Scale: 1 : 5000.

adsorption capacity of bentonite, whereas the heat treatment improved it.

The high COD removal yield, reported in Fig. 1, indicates that the thermal treatment provided MgOCaO with satisfactory adsorption capacity. The adsorption yield progressively decreased with increasing O/W ratio, indicating an excess of pollutant with respect to the adsorbing material. In addition, as expected, the soluble oil was adsorbed more effectively than the insoluble one,
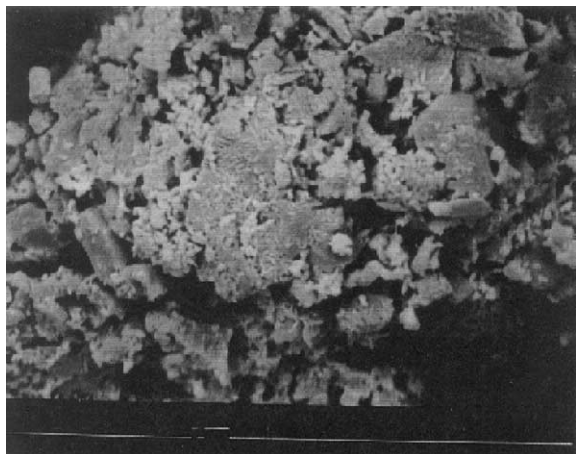
Fig. 3. Micrograph of a dry sample of $MgO \cdot CaO$. Scale: $1 : 5000$.

Fig. 4. Isotherms of adsorption of (●) soluble and (■) insoluble oils with $MgO \cdot CaO$ and of (○) soluble and (□) insoluble oils with $MgO \cdot CaO$ activated with HCl.

over the whole O/W range, because of its lesser content in organic substances.

A different behaviour is evident in the same figure for the adsorbent treated with HCl with regard to the different pollutants, which also seems to be associated with the appearance of a gel layer after the chemical activation. In fact, the yield of COD removal from soluble oil exceeded 0.90, over the whole range of O/W investigated in this study. After treatment with coalescent, the solid phase separated rapidly from the aqueous one, with the formation of a clear upper aqueous layer and the settling of oil adsorbed onto the material. On the contrary, no significant improvement was detected for the adsorption of water-insoluble oil, as demonstrated by an increase in the removal yield from 0.40 up to only 0.44 at $O/W = 0.02$.

On plotting the COD amounts adsorbed per unit substrate against the equilibrium concentration, the adsorption isotherms of Fig. 4 were obtained for either the emulsified or the insoluble oils treated with both adsorbents. In all cases, the linear trends can be well described ($r^2 = 0.946 - 0.998$) by the Freundlich model:

$$q = kC^{1/n}, \qquad (2)$$

where q is the amount of adsorbed pollutant, k the Freundlich affinity parameter, C_{eq} the oil equilibrium concentration, and n the exponential Freundlich coefficient. The values of k and n (Table 2), estimated for the different adsorbents and oils from the straight lines of Fig. 4, are indicative, in general, of a good adsorption power of the tested adsorbents and, in particular, of a higher adsorption capacity of the material activated with HCl. In addition, the soluble oil was adsorbed very effectively, whereas insoluble oil was adsorbed only partially. Such behaviour cannot be simply explained with the lesser content of the soluble oil in organic
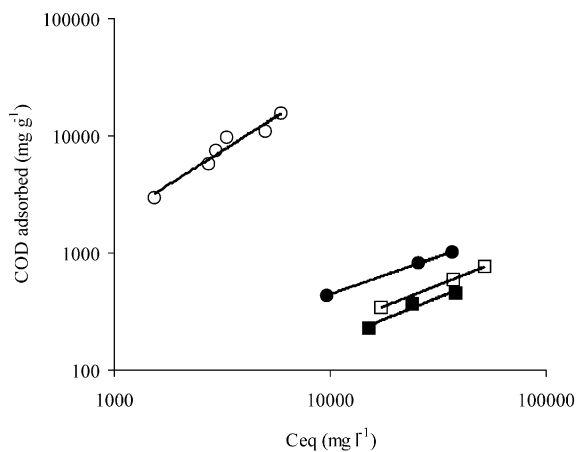
Table 2
Freundlich parameters estimated for the adsorption of either emulsified or insoluble oils

	$MgO \cdot CaO$	$MgO \cdot CaO$ activated with HCl
Emulsified oil		
K	1.21	0.62
$1/n$	0.64	1.16
r^2	0.998	0.946
Water-insoluble oil		
K	0.18	0.28
$1/n$	0.74	0.72
R^2	0.958	0.998

substances, but also with what is taking place on the surface of the adsorbent during its chemical activation.

As proposed by Shimizu et al. [21], the organic compounds of soluble oil, which are surrounded by an envelope of structural water, are apolar and therefore only able to link the adsorbent through weak Van der Waals forces. So, the better results obtained in this work for the soluble oil with respect to the insoluble one, could be ascribed to the interaction between water molecules and functional groups of the adsorbent, that would improve their capability to attract the organic substances. This effect could have been stronger when the adsorbent activated with HCl was used, because of the development of a gel layer with improved sorption properties with respect to the material not activated in this way. According to this hypothesis, the treatment with HCl solution could have made the adsorbent more nucleophilic through the reactions:

$$A = O + 2\,HCl \rightarrow ACl_2 + H_2O, \qquad (3)$$

$$A = O + H_2O \rightarrow A(OH)_2, \qquad (4)$$
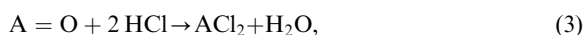
where A indicates Mg or Ca, and, then increased its adsorption power.

This improvement was nearly negligible with regards to the insoluble oil because of the little chemical affinity between polar adsorbing groups and apolar organic substances. For this reason, nearly the same yield of COD removal was obtained for this pollutant with both adsorbents. On the other hand, it became significant when the emulsified oil was treated, likely because the increases in both nucleophilia and electron affinity of the adsorbent, due to the substitution of some oxygens with chlorines, enlarged the distance from the adsorbent surface at which the envelope of structural water surrounding the organic molecules felt its adsorption power.

The physical characteristics of these adsorbents, whether submitted or not to HCl activation, have already been compared in Table 1 with those of "raw" dolomite. As previously mentioned, MgO CaO has larger specific surface area and average pore diameter as well as higher total porosity with respect to starting dolomite. The treatment at high temperature destroyed dolomite structure by the transformation of carbonates into their respective oxides. As a consequence of this phenomenon, a significant number of new pores and sites available for the oily particles adsorption could have been originated by CO_2 development.

The activation with HCl decreased the specific surface area and total porosity of the adsorbent by 36% and 39%, respectively. These values suggest that the formation of a gel layer according to Eq. (4) could have caused alterations in the size and pores distribution, enlarging the average pore diameter. From such a modification, one would expect a decrease in the amount of adsorbed pollutants, as a consequence of the reduction of the surface available for adsorption. However, the results obtained in this study showed an opposite trend, especially in the case of soluble oil, thus supporting the hypothesis formulated above about the increase in the adsorption power consequent to chlorination (Eq. (3)).

4. Conclusions

Adsorption tests performed with $MgO \cdot CaO$ from dolomite calcination demonstrated that this waste material can favourably be employed as an adsorbent for the removal of oily substances. Two different kinds of exhausted oils were submitted to adsorption tests: a water-insoluble lubricating oil utilised for automotive engine and a water-soluble cutting oil employed as coolant for machine tools.

Maximum COD removal yields with this adsorbent were 0.40 and 0.60 for insoluble and soluble oils, respectively. An enhancement of the adsorption power

of this material was obtained by treatment with HCl, which caused significant changes in its surface. The COD removal yield for soluble oil increased remarkably (from 0.60 up to about 0.95), while only a little improvement was observed for insoluble oil (from 0.40 up to 0.44).

On the basis of these results and by comparative microscope examination of the morphologies of both dolomite and MgO CaO, the following mechanism has been proposed for the adsorption of emulsified oils on this material: the apolar fraction of the oil is mainly adsorbed by Van der Waal forces, which are stronger when chlorine atoms substitute oxygen atoms, as it took place when the adsorbent was activated with an HCl solution.

The results of this work demonstrate the possibility of employing the products of dolomite thermal treatment as adsorbents, mainly when submitted to a suitable chemical activation treatment, and suggest these recycling materials as an interesting alternative to the most common adsorbents, especially for the removal of exhausted water-soluble oils.

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