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SCIENTIFIC PAPER

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REMOVAL OF MINERAL OIL AND WASTEWATER POLLUTANTS USING HARD COAL

This study investigates the use of hard coal as an adsorbent for removal of mineral oil from wastewater. In order to determine the efficiency of hard coal as an adsorbent of mineral oil, process parameters such as sorption capacity (in static and dynamic conditions), temperature, pH, contact time, flow rate, and chemical pretreatment were evaluated in a series of batch and continuous flow experiments. There were significant differences in the mineral oil removal for various pH values examined. The adsorption of mineral oil increased as pH values diverged from 7 (neutral). At lower temperatures, the adsorption was notably higher. The wastewater flow rate was adjusted to achieve optimal water purification. Equilibrium was reached after 10 h in static conditions. At that time, more than 99% of mineral oil had been removed. At the beginning of the filtering process, the adsorption rate increased rapidly, only to show a minor decrease afterwards. Equilibrium data were fitted to Freundlich models to determine the water-hard coal partitioning coefficient. Physical adsorption caused by properties of the compounds was the predominant mechanism in the removal process.

Key words: hard coal; mineral oil; adsorption; water treatment.

One of the major environmental issues nowadays is the vast and widespread occurrence of oil in the soil, industrial wastewater and ground water. Oils (both mineral and synthetic) are considered persistent environmental contaminants and many of them are suspected of being carcinogenic [1,2]. Hence, they are included in the US-EPA lists of priority pollutants. The EEC Directive 76/160/EEC limits the concentration of oil in water for human consumption to 0.3 $\mu g \cdot l^{-1}$.

The removal of oily pollutants from wastewater poses a problem, particularly when they are present in low concentrations, such as in industrial water. Over the recent years, the increasing attention has been given to the quantity of other toxic materials found in these waters. Because of its simplicity, reliability and its inexpensiveness, the adsorption technology is extensively used in oil removal. Traditionally, activated carbon has been widely used as an adsorbent for removing oil. Many types of other adsorbent materials such as bentonite [3], kaolinite [4], fractured chalk [5], fulvic acid [6], humic acid [7], wood [8,9], surfactants [10], surfactant-modified alumina [11], have been studied as alternatives for removing HOCs contaminants. All these adsorbent materials have specific advantages and limitations, so the need to develop low-cost adsorbents remains. This study examines the applicability of hard coal as a low-cost material for adsorbing oil from industrial wastewater.

This study was done to determine whether the hard coal can be used as an adsorbent material for removing oil from wastewater. In a series of batch and continuous flow experiments, the effects of important factors such as pH, contact time and pollutant concentration on the adsorption capacity of hard coal were examined.

EXPERIMENTAL

The hard coal used in this study was supplied by Vrška Čuka coal mine in Serbia. The material was sieved to a grain size of 1-5 mm before being used in the adsorption experiments. Table 1 shows some of its chemical and physical characteristics, which were determined beforehand.

All samples of wastewater used in this study were taken from the “Petrohemija” plant in Pančevo,

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Table 1. Physicochemical properties and granulometric characteristics of the hard coal sample used in this study

Physical characteristics	Hardness (Moss)	Specific weight (kg/m^3)	Sorption medium		Sorption CCl_4 (%)	Specific surface m^2/g
			Acid	Base		
Hard coal	4	725	5.90	2.46	3.88	0.7

Sieve (mm)	2	1.6	1.0	0.5	<0.5
Hard coal (%)	6.5	80	11.8	0.9	0.1

Chemical composition, %	Ash	C	N	H	S	Moisture
Hard coal	4.10	90.00	1.05	3.60	0.81	0.80

Serbia. Before any sampling, glassware was previously cleaned with nitric acid; water free of organic traces (Milli Q) was used in all procedures performed.

The amount of oil in oily wastewater before and after the adsorption experiment were determined by IR spectrophotometry at 3.28, 3.40 and 3.50 μm, according to JUS H.Z1.151 standard, using CCl_4 to extract the oil.

The effect of sorbent weight

Hard coal, granulated from 0.6 to 1.6 mm, was used to determine the static sorption capacity. The oil content was measured to be 7.50 ppm, while the volume of oily wastewater was 100 ml. During the experiment, hard coal weight was changed from 10 to 100 g. Once oil was extracted from the wastewater using CCl_4, the initial oil concentration was determined by IR spectral analysis. After filtration, determined oil concentrations were found to be 3.8, 2.2, 1.8 and 1.8 ppm, while hard coal weight were 10, 20, 50 and 100 g, respectively.

In the same experiment, a hard coal sorption capacity was found to be 6.0 mg oil/100 g sorbent, which seems to be less than a half of the sorption capacity value obtained by activated coal (11.3 mg oil/100 g sorbent) or sepiolite (12.4 mg oil/100 g sorbent). These values are obtained at room temperature, atmospheric pressure and pH value of 6.80–7.30.

The effect of temperature

Sorption is a dynamic process, involving both adsorption and desorption. The adsorbate molecules are in constant motion; they are attracted by the surface force and attach to the surface of the sorbent. The increase in temperature speeds up the Brownian motion, requiring a stronger force to keep the molecules adhered to the surface (the higher the temperature, the higher the speed of the molecules' Brownian motion, reducing the possibility of adsorption of these molecules).

The filtration process can be explained in a similar manner. The oil viscosity decreases as the temperature rises, reducing the possibility of oil removal. In addition, the higher the temperature, the faster will the already separated oil drain off the filter be. Finally, as temperature increases, the oil solubility increases as well, decreasing the separation of the oil from water. The measured sorption capacity values for temperatures 22, 54 and 66 °C were 6.0, 3.8 and 3.2 mg oil/100 g sorbent, respectively.

The effect of pH

Batch experiments using 100 ml of oily water were performed at different pH values. The oily wastewater was adjusted to initial pH values of 3.0, 6.8 and 10.5 by addition of concentrated H_2SO_4 or NaOH. After the pH adjustment, 100 ml samples were analyzed to determine the initial oil concentration. Subsequently, 10 g of hard coal was added to the glass flasks containing 100 ml of oily wastewater. One sample of oily wastewater was used without pH adjustment (6.8). The blank was prepared by adding 10 g of hard coal to 100 ml of Milli-Q water free of organic traces to check whether the adsorbent could release any oil into the aqueous solution. The samples of oily wastewater, with the added hard coal, adjusted to different pH values (3.00-10.50), were examined statically for 1 h. The measured sorption capacity values, for both pH values 3.0 and 10.5 were 7.5 mg oil/100 g sorb., and 6.1 mg oil/100 g sorb. for pH value of 6.8.

Effect of contact time

The effect of contact time was examined by passing a certain amount of oily wastewater through the batch-flow filtration column (85 mm diameter, 380 mm hard coal height). The initial concentration of oil was extremely high (6500 ppm). Hard coal granulation was 0-3 mm. Oily wastewater was in constant contact with hard coal; during sampling, the wastewater passed through the bed of hard coal, starting at the bottom of filtration column upwards. Dynamic contact was thus simulated, with very low volume flow, in order to determine the contact time data for the sorption process. The results of these measurements are shown in Fig. 1.

It is obvious from Fig. 1 that the largest amount of mineral oil was adsorbed very rapidly, at the beginning of the process. An hour later, the oil concentration was decreased to 2.5 ppm, only to decrease further to 1.2 ppm 12 h later.

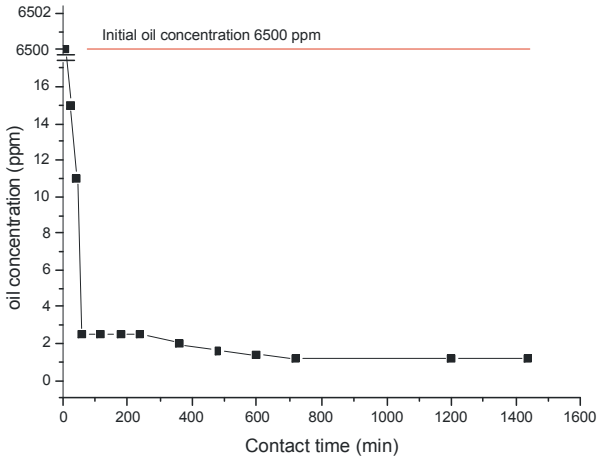

Fig. 1. Decrease in oil concentration in time.

The effect of the amount of wastewater used

The second set of experiments was very similar to the one already described, except that, the amount of wastewater passed through the column at the end was the same as the amount initially added to the filter column. The samples were taken each hour, for a total of 14 measurements. The results are presented in Fig. 2.

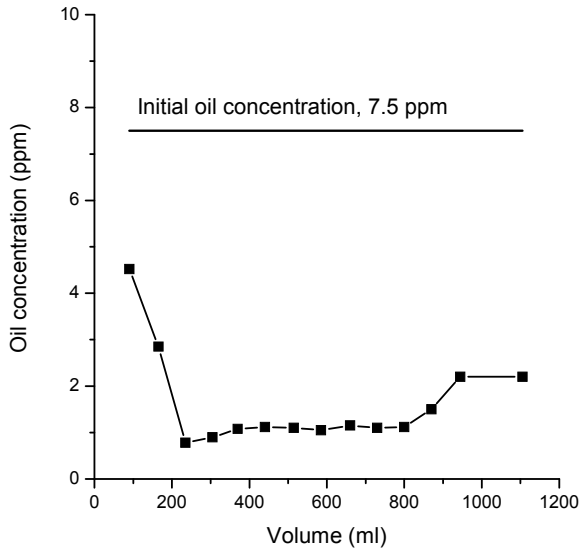

Fig. 2. Oil concentration vs. the amount of oily wastewater passed through the column.

The dynamic properties of the hard coal shows that the removal of oil from oily wastewater is close to constant (around 1 ppm), and the ability to remove oil is preserved for a long time.

The effect of wastewater flow

The initial oil concentration in oily wastewater was found to be 7.5 ppm. A continuous flow filtration column (85 mm diameter, 380 mm hard coal height) was loaded with hard coal (granulated 0.5–1.6 mm). The volume flow was set to 350 ml·h^{-1} and the oil concentration at the outlet of the column was 2 ppm. When the volume flow was decreased to 300 ml·h^{-1}, and subsequently to 260, 200 and 150 ml·h^{-1}, the oil concentration at the outlet dropped to 1.7, 1.5, 1.4 and 1.3 ppm, respectively. By decreasing the volume flow to the 100 ml·h^{-1}, the oil concentration dropped to 1.1 ppm. It is very important to note that a certain time must pass to allow the filter column to achieve its optimum performance efficiency, as it was shown in the previous experiment as well.

It seems evident that the adsorption takes place at the surface of hard coal, as hard coal grains are not porous (Table 1). Hard coal is a high-rank coal, and is a complex material predominately made of carbon (90 wt.%), which offers a relatively non-polar environment into which a hydrophobic compound may escape without undue competition with water. Due to high interfacial tension between hard coal particles and mineral oil, oil molecules are attracted by the planar surface of hard coal particles. As a result, a thin monolayer of mineral oil is formed on the surface of hard coal particles. However, during the filtering process, due to high adhesion forces between mineral oil layers, a mineral oil multilayer forms.

A thin film is formed on the surface of each hard coal grain as the grains are soaked in oily wastewater. The efficiency of the oil removal increases with time, as a multilayer film forms on the surface of hard coal grains, since the adhesive force is strong between the layers of oil. Smaller grains adhere to larger grains during the filtration process, forming agglomerates, and the space between these grains is filled with a thin film of oil, separating the oil from the oily wastewater.

Effect of addition of other filtration media

This experiment was performed using two filtration columns, as described above. The first column was packed with hard coal (granulated 1.6 to 2 mm). Sulfuric acid was added to oily wastewater (initial mineral oil concentration 42 ppm) that was passed through this column, in order to adjust the pH value to 3.0-3.5. The other column was also packed with hard coal (granulated 1.6 to 2 mm). On top of the coal in this second column, Ca $(OH)_2$ was added in the mass ra-

tio of 10:1. The filtered water from the first column was passed through the second column. After passing through the second column, the filtered water pH value was set to 7.5-8.0, and the concentration of oil was dramatically reduced. The results of this experiment are shown in Fig. 3.

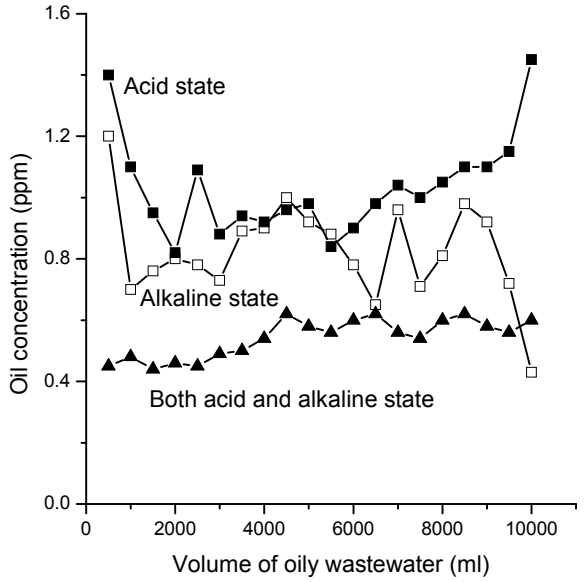

Fig. 3. Oil concentration in filtered water vs. amount of wastewater volume in acid, alkaline and combined acid and alkaline processes.

The efficiency of the oil removal, using acid and alkaline processes, as well as the efficiency of the combined acid and alkaline process can be seen from Fig. 3. The alkaline process seems to be more appropriate for filtration, as it can also be seen from the before mentioned experiments. Notably, the best result is obtained using the combined process, which is very important since this filtered water is neutral, and poses no threat to the environment when released.

The dynamic sorption process

Hard coal sorption efficiency increases after the start of the sorption process. When the sorption process starts, oil molecules are attracted by planar surface of hard coal particles, forming a monolayer film on their surfaces. During the first stage of this process, oil sorption is mainly controlled by the interfacial tension between oil molecules and hard coal surface. Our experiments show an increase of the oil removal efficiency in the filtration process, in comparison with batch experiments. The filtration column was packed with hard coal granulated at 0-3 mm. Oily wastewater was then passed through the column. Three different samples of wastewater were included in this experiment, with 38, 15 and 5 ppm of the initial mineral oil concentration, respectively. The results obtained by this experiment are presented in Fig. 4.

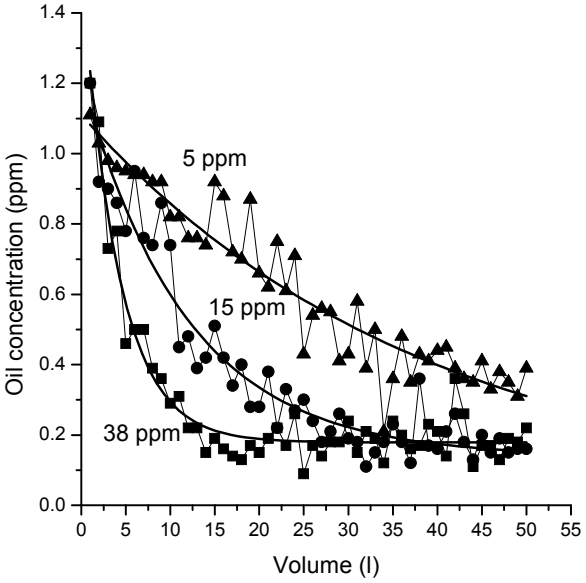

Fig. 4. Oil concentration in filtered water vs. amount of wastewater volume, following a chemical pretreatment of wastewater.

By comparing the efficiency of the filtration process presented in Fig. 4 with batch experiments previously described, it is clear that the efficiency in this process has multiplied more than 10 times, with the increased filter material life. In this experiment, an oily wastewater flow varied from 2 to 4 $l \cdot h^{-1}$, but the filter column efficiency remained unchanged.

Hard coal sorption capacity, according to all these experiments, is determined to be more than 5,6 g oil/kg hard coal (granulated 0-3 mm).

RESULTS AND DISCUSSION

pH effect

The sorption of mineral oil on hard coal was studied at pH 3, 10.5 and non-adjusted pH (6.8) to determine the optimum pH for the sorption of mineral oil. The amount of mineral oil removed was calculated by determining the initial mineral oil concentration and the concentration remaining in the solution after 1 h of contact time. The analysis of the mineral oil concentration in a blank solution showed that there was no leaching of these compounds from the adsorbent.

The experiments show that different initial pH values of the oily wastewater evaluated have no significant effect on the adsorption process of mineral oil. Differences in oil removal between pH values of 3.0

and 10.5 were under 15%. This is due to the properties of this chemical compound, since oil is chemically very inert as its composition (mainly alkanes) gives it this chemical stability. As a result, heavier oils with longer chains are less affected by pH. Furthermore, these compounds do not have ionizable or hydrophilic groups that can be influenced by the pH value. Because the sorption of oils onto hard coal is a hydrophobic interaction, the adsorption of compounds with higher molecular mass is affected, to a minor degree, by the pH values studied, as it was expected. It seems that adhesion or the interfacial tension between mineral oil and hard coal surface is the predominant process.

Effect of contact time

Fig. 1 shows the adsorption data for mineral oil uptake *vs*. contact time. As shown, adsorption increases with contact time. The results show that mineral oil was removed rapidly at the beginning of the process, and most of the sorption occurred within the first hour of contact. At a contact time of 1 h, the concentration of oil was very close to 2.5 ppm. After this time, the uptake efficiency decreased, gradually approaching equilibrium. Equilibrium was reached after 12 h of contact time, with mineral oil concentration of 1.2 ppm (mineral oil removal of almost 99.99%).

As indicated by these results, the adsorption appears to be governed by two transport processes. During the first stage, mineral oil is rapidly adsorbed onto the hydrophobic hard coal surface through adhesion interactions, for 1 h. In the second stage, a slower migration of mineral oil to less accessible sites within the hard coal matrix can be observed in the following 11 h. During the second stage, mineral oil adheres to the mineral oil layer formed on hard coal particles. Adhered oil droplets reduce the flow of oily wastewater through hard coal bed in the column and prolong the contact time, which is favorable for the mineral oil removal. Therefore, a large amount of mineral oil is expected to be progressively adsorbed by the adsorbent matrices as contact time increases.

Once a monolayer film of mineral oil had formed on hard coal particles, the removal of mineral oil from wastewater increased due to the increase in the adhesion surface. The mineral oil adhesion takes place as well, and the agglomerates of mineral oil droplets form in the space between hard coal particles. The uptake efficiency was dependant on the time that the mineral oil remained in the solution with hard coal.

Adsorption isotherm

Different ratios of oily wastewater/hard coal concentrations were examined in glass flasks to determine the adsorption capacity of the adsorbent material. These experiments were performed on 100 ml portions of oily wastewater with pH values of 3.0, 6.8 and 10.5, with 10 g of added hard coal, exposed for 1 h of contact time. The results obtained were used to plot an adsorption isotherm.

The Freundlich isotherm is the most widely used equation for interpretation of sorption equilibrium data for mineral oil diluted in wastewater. The following equation represents the logarithmic form of this equation:

$$\log q = \log K + \frac{1}{n}\log c_W \quad (1)$$

where: q is the mass of sorbed mineral oil per weight unit of adsorbent ($mg \cdot kg^{-1}$), c_W is dissolved mineral oil concentration ($mg \cdot l^{-1}$), n is the measure of linearity, and K is Freundlich constant.

The Eq. (1) postulates either a) linear sorption, meaning that the overall sorption process is linear, described by a linear isotherm (n = 1), or b) the relative concentration variation, dc_W/c_W, is small enough to guarantee that the relative K variation, dK/K, is small as well [13] and the values of K decrease as the residual concentration c_W in the aqueous phase increases. From Fig. 5 and Eq. (1), the evaluated value of K is 2.70.

Fig. 5 shows the fitting of the isotherm data to the logarithmically transformed Eq. (1). The isotherm is found to be almost linear (n = 1). According to literature data, the sorption of mineral oil to hard coal is often characterized by linear isotherms in which the ratio of sorbed and aqueous oil concentration is independent of concentration [12,13]. There have been numerous reports in references of environmental sorbents exhibiting non-linear sorption isotherms [3--5,8,9,14,15].

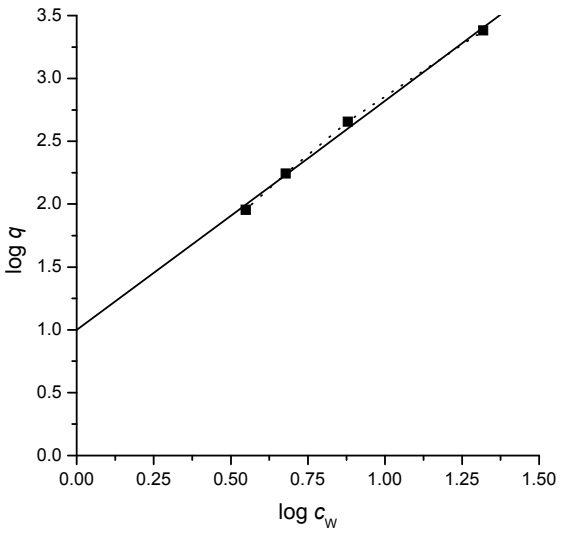

Fig. 5. Isotherm data logarithmically transformed to Eq. (1).

In accordance with these results, the studies carried out in different environments suggest that, in addition to the pollutant's physicochemical properties and concentration, the properties of the adsorbents play an important role in the estimation of mineral oil sorption. In addition, environmental conditions affect the adsorption process also [6,7,14,16-24].

In spite of the low adsorption capacity of hard coal compared to other adsorbents (especially activated carbon), its removal percentages at the concentrations evaluated, and those found in the environment, suggest that this material can be useful for abating mineral oil pollution. This inexpensive material is available in large quantities. Due to its low cost, it may be used as an ecological alternative in permeable reactive barrier applications. After use, hard coal can be disposed into the environment without any treatment or regeneration.

CONCLUSIONS

The influence of different parameters on the adsorption of mineral oil by hard coal was evaluated.

The pH showed no significant effect on the adsorption of mineral oil. Its removal rate rose to 95.9% at pH 3.0 and 10.3, while the removal rate at pH 6.8 was only 78.2%. This phenomenon can be explained by a decrease in the polarity of oil agglomerates as pH decreases, which allows the matrix to adsorb most of the mineral oil.

The contact time is an important factor in the adsorption of mineral oil by hard coal. Equilibrium was reached after 12 h. The adsorption was controlled by two transport processes; one fast (2 h) and one slow (10 h).

The removal percentages at the concentrations evaluated, and at those found in the environment, suggest that hard coal can be useful for abating mineral oil pollution. This material can be used as a low-cost alternative in reactive barrier applications. The vast availability and low cost of hard coal make it a promising candidate for use in pollution remediation, both for industrial wastewater and groundwater.

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