TREATMENT OF OILY WASTEWATER BY ADSORPTION USING ANHTRACITE

Jovica Sokolović, Rodoljub Stanojlović,
Suzana Stanković, Vojka Gardić

Abstract: *Oily waste water is wastewater with oils and fats, which come from various industries and production processes. Waste oil and any oil containing wastes have a high potential to pollute and degrade the environment especially water and soil. As such, they represent a major environmental problem. To protect the environment, oily wastewater treatment is unavoidable.*

Adsorption process is one of the effective methods for treatment and removing oil from oily waste water. Based on the positive experiences, research has performed on the application of the anthracite coal mine „Vrska Cuka" Avramica in the purification of oily wastewater. Increased efficiency of coal as an adsorbent of mineral oil is achieved by application of studied coal materials. Adsorption capacity of Serbian anthracite is great, and the same can be obtained at much lower prices.

Keywords: *oil, wastewater, Copper Mine Bor, adsorption, anthracite, Vrska Cuka.*

1. Introduction

Due to urbanization and industrial development, one of the most serious environmental issues are waste oil and oily waste water. Waste oils have a complex chemical composition and contain organic (fats, lubricants, cutting liquids, heavy hydrocarbons (tars, grease, crude oils and diesel oil), and light hydrocarbons (kerosene, jet fuel and gasoline) [1] and inorganic compounds, with about 20 % all the known chemical elements.

Water pollution by waste oil has left an undesired impact on the environment. Further risks to human health may arise, e.g. the risk of skin cancer from skin contact with used motor oils, probably due to PAHs. A proper collection and treatment as well as the mitigation of any spills are therefore essential for the successful management of waste oils. At the same time waste oils (and oil containing wastes) are an significant resource [2].

2. Framework for management of waste oils / oil wastes

2.1. EU Waste Framework Directive – waste oil

Waste oils are now regulated by Directive 2008/98/EC on waste [3] and repealing certain directives (including Directive 79/439/EEC on waste oils).

According to Article 3(3) of the Directive, waste oils are waste oils are *"any mineral or synthetic lubrication or industrial oils, which have become unfit for the use for which they were originally intended, such as used combustion engine oils and gearbox oils, lubricating oils, oils for turbines and hydraulic oils." (including Directive 79/439/EEC on waste oils).*

"Regeneration of waste oils means any recycling operation whereby base oils can be produced by refining waste oils, in particular by removing the contaminants, the oxidation products and the additives contained in such oils" (Article 3(18) of the Directive.

2.2. Serbian legal framework for waste oil

Basic legal requirements regarding the management of waste oils are given by the Serbian Law on Waste Management (Official Herald RS, No 36/09 and 88/10). Detailed provisions were laid down in 2010 with the adoption of the Governmental order on conditions, methods and management procedures of waste oils (Official Herald RS, No 71/2010). Technical requirements for incineration and co-incineration of waste oil are stipulated by the Governmental order on conditions, method and procedure of thermal waste treatment (Official Herald RS", No.102/2010).

3. Treatment of waste oil and other oil wastes

Environmentally sound and sustainable waste oil management requires an integrated system of waste oils collection, recycling and final disposal. Waste oils cover a wide range of quality, from high grade oils with only few contaminates to waste streams with only a low oil content.

Because of its characteristics, waste oil (mineral and synthetic) are classified as hazardous waste and are considered potential environmental pollutants, especially if we take into account the total amount of waste oil are generated.

According to data available for several European countries approximately 50 to 70 % of oils and lubricants market input are collected as waste oil [2]. The remaining part is either consumed, lost in any oil containing wastes (e.g. interceptor sludges, oil filters, etc.) or has been dissipated in the environment. With an annual consumption of

50000 tonnes of oils and lubricants in Serbia the generation potential of waste oil is estimated to account for 25000 to 37,000 tonnes per year [2].

Many oil containing waste streams (oil-water mixtures, separator content, recovered oil from emulsions) have a varying composition and are therefore not fit for recycling. Such wastes should preferable be recovered and converted into secondary fuel. Whereas for high grade oil wastes the profit gained from recycling may cover or even exceed the costs of collection and pre-treatment, the proper treatment of low grade oil containing wastes (such as water-oil separator content) may exceed the value of the oil recovered.

Several types of oil wastes have to undergo specific pre-treatment before they can be used as an input in re-refining or energy recovery (incineration) processes. Figure 1 below gives an overview on treatment options for oil wastes.

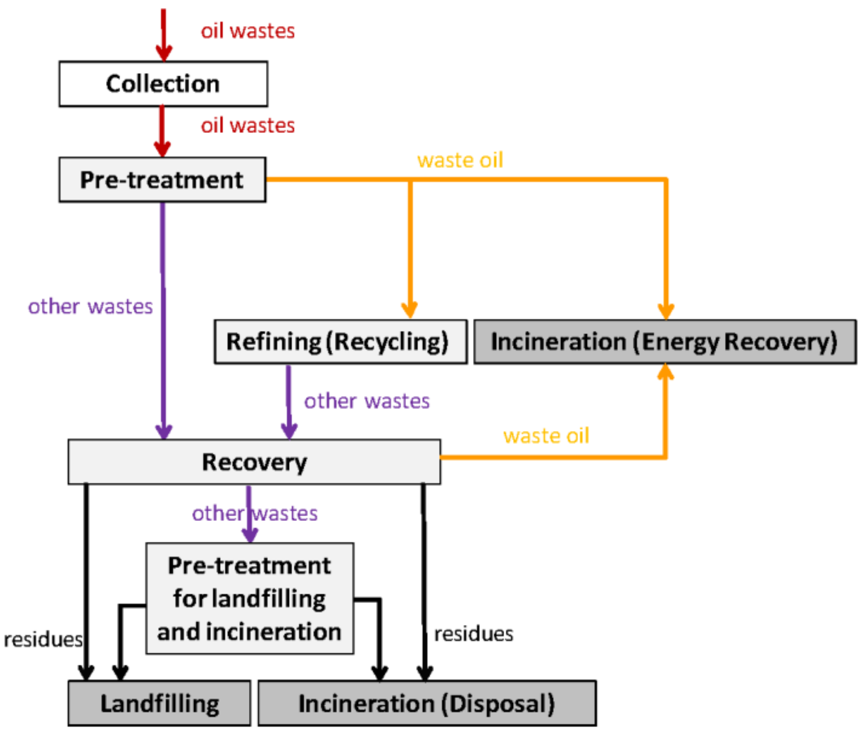

Figure 1. Overview on the main treatment steps for oil wastes and waste oil [2]

The proper management of various types of waste oil is not only environmentally, but also economically important. After the exploitation, waste oil can be used as an alternative source of energy (incineration) or recycling (re-refinement) in the base oil.

Also, removal of oils and fatty substances polluting from the waste water is a problem, especially when they are present in small concentrations, such as oily waste water.

4. Oily wastewater

Oily wastewater is one of the most serious environmenta issues generated by production in oil fields, oil refineries, ferrous and non-ferrous metallurgy, metal processing, mineral processing and chemical industries, as well as thermal energy and mining systems. Such widespread use of lubricants in these industries means both large dispersion of waste oils and indicate possible contamination of water and soil.

The concentration of oil and fat in the wastewater is not always an indicator of the level of pollution in the cases of periodic discharges or the dilution of other waste water comes to a rapid disturbance.

The Serbian environmental law stipulates that disposed water should not contain more than 10 mg/l of oil and this requirement is becoming more enforced as damaging environmental effects from oily wastewater become more apparent. Due to hazards of oil field effluents on environment, treatment is necessary before disposal [4].

The treatment of oily waste water is important not only from an economic view point but also in terms of ending the pollution of water resources [5]. Treatment of oily waste water is performed by various methods and the degree of removal of oil mainly depends on the concentration of oil, the physical properties of oil and oil droplet size. The oil droplets in effluents contain spilled oil, dispersed oil, emulsified oil and dissolved oil [6].

The most commonly used methods for treatment of oily wastewater, before their disposal, include mechanical (skimming), physical (gravity separation), chemical (neutralization), physicochemical (i.e. flotation, adsorption, membrane process, coagulation and flocculation, electrochemical, emulsion breaking), biochemical (bilogical treatment, activated sludge). [1, 4-7]

Emulsified oils with oil droplets smaller than 20 μm can be effectively removed from waste water by adsorption [1].

4.1. Adsorption and adsorbing materials

Adsorption process is the physical adhesion of the polluting chemicals onto the surface of a solid [5]. The adsorption mechanism is complicated and, although the attraction is primarily physical, is a combination of physical, chemical, and electrostatic interactions between the adsorbent and the organic compound [7].

A wide range of adsorption materials, such as activated carbon, bentonite, peat, sand, coal, fiberglass, polypropylene, amberlite, organoclay, and attapulgite [5] have been examined for oily wastewater treatment. Traditionally, activated carbon has been widely used as an adsorbent for removing oil [8].

Due to low efficiency and high cost of activated carbon for oily wastewater treatment [10], the possibility of using inexpensive materials as alternatives was explored by many researchers in the past years [9]. The development of low-cost adsorbents has led to the rapid growth of research interests in this field.

A detailed review of the literature, it was observed that, anthracite as natural, inactivated adsorbent and studies its effectiveness as adsorbents for the removal of oil from wastewater is not insufficient attention is paid.

4.2 Previous researches using anthracite as an adsorbent for treatment of oily wastewater

Anthracite is the energy source of high level of carbonation, whose ability to adsorb known since ancient times. Coal anthracite particles absorbed oil droplets from the waste water, especially the smaller sized droplets and the emulsified oil. The adsorption of oil depends on three processes: diffusion of oil molecules into the substrate; capillary action of the oil at the fiber structure/substrate interface; and, aggregation of oil in cavities such as pores, microcracks and uncovered interfaces [5].

Li et al. [5] showed that coal type and particle size significantly affect the adsorption of oil from oily wastewater. The adsorption capacity of hard coal is much higher than that of brown coal and lignite for all size class. The higher adsorption capacity is obtained when the fine class for all types of coal. The contact time required to achieve the adsorption equilibrium is shorter than in anthracite brown coal and lignite. The adsorption capacity of anthracite decreases with increasing pH of the pulp. The adsorption of oil on anthracite follows the Freundlich isothermal adsorption law. The results indicate that the activation process increases the adsorption capacity of coal, which is the consequence of increasing the specific surface area and internal structure changes.

Simonovic et al. [8] were investigated 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. The results showed that anthracite is very efficiently absorbs and removes oils and phenols from the oily wastewater. 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.

Recent studies of Sokolovic et al. [11] was focused on investigating the potential application of anthracite from coal mine Vrska Cuka, Serbia to purification of oily waste water from Copper Mine Bor, Serbia. The Copper Mine Bor generated significant amounts of oily wastewater are waste water with oils and fats and such as represent a major environmental problem. The treatment of oily waste water is important not only from an economic view point but also in terms of ending the pollution of water resources.

The experimental methods which were employed in this investigation included batch studies. Coal was added to oily waste water as an adsorbent. The ration of solid-liqiud system, absorption time, pH value, initial oil concentration and coal type were investigated.

Three types of anthracite were used to treat oily wastewater. Fine waste coal below 1 mm was used as adsorbent, it is obvious that it is more inexpensive and its efficiency for removal of oil in water has been compared with raw coal and separated coal (5 % ash). The removal efficiencies of these materials were compared to each other.

The results indicate that oil absorption by a fine waste coal increases for adsoption time of 1 h and then gradually tends toward an equilibrium value. The oil adsorption of anthracite decreases slightly as the pH increases from 3 to 7 and increases slightly as the pH increases from 8 to 11. Also, the lower and the higher initial pH of oily water (up to a certain limit) to affect an increase in the adsorption capacity.

The degree of adsorption is higher when the adsorption process is performed by applying quality coal. The degree of adsorption using the fine class of waste coal is 70.37 %, while for the same class using the separated coal the value of 79.26 %.

The results showed that separated coal performed some better properties in removal of oil. Thus molecules of hydrocarbons from the oil much easier to adsorb and bind to the surfaces separated coal and the effects of treatment of oily water have been higher. This also increases the adsorption capacity as compared to raw coal, and the waste of 10 to 15 %.

Also, the oil can first be separated from the waste water where the fine coal is used as an oil adsorbent and then the fine coal-oil mixture is separated from the waste water by flotation economically and with high efficiently. As a result, oil removal from waste water was successfully separated. Therefore, results confirmed that oily waste water can use as effective collector for coal flotation od raw and waste coal from the anthracite coal mine „Vrska Cuka".

5. Conclusion

Oily wastewater is one of the most serious environmental issues. The latest results of the treatment of the oily wastewater from Copper Mine Bor by fine waste coal from Coal Mine Vrska Cuka as an adsorbent indicate showed that anthracite efficiently absorbs and removes oils and fats from the oily wastewater.

Oil is absorbed to the coal anthracite particles and then separated from the water through flotation. Fine oily classes of waste coal can be used as an energy source. This allowed economical and highly efficient separation of oil from the waste water.

Treatment of these effluents may result in improved water quality, oil recovery, water reuse, protection of downstream facilities and environmental protection.

6. Acknowledgements

The authors are grateful to Ministry of Education, Science and Technological Development of the Republic of Serbia, for the financial support (project TR 33007 and TR 33038).

7. Bibliography

Srinivasan, A., and Viraraghavan, T. (2010). Oil removal from water using biomaterials. Bioresource technology, 101 (17), 6594-6600.

Ministry of Environment and Spatial Planning, Serbian Waste Management Plan for Oil Wastes, Draft version 2, 2012.

Directive 2008/98/EC on waste (EU Waste Framework Directive) of the European Parliament and of the Council on waste, 2008.

Okiel, K., El-Sayed, M., and El-Kady, M. Y. (2011). Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. Egyptian Journal of Petroleum, 20 (2), 9-15.

Li, X., Zhang, C., and Liu, J. (2010). Adsorption of oil from waste water by coal: characteristics and mechanism. Mining Science and Technology (China), 20 (5), 778-781.

Li, X. B., Liu, J. T., Wang, Y. T., Wang, C. Y., and Zhou, X. H. (2007). Separation of oil from wastewater by column flotation. Journal of China University of Mining and Technology, 17 (4), 546-577.

United States Environmental Protection Agency (USEPA), Office of Water, Development Document for Proposed Effluent Limitations Guidelines and Standards for the Centralized Waste Treatment Industry, Volume I, Chapter 8-Wastewater Treatment Technologies, 1998.

Simonovic, B. R., Aranđelovic, D., Jovanovic, M., Kovacevic, B., Pezo, L., and Jovanovic, A. (2009). Removal of mineral oil and wastewater pollutants using hard coal. Chemical Industry and Chemical Engineering Quarterly, 15 (2), 57-62.

Ibrahim, S., Wang, S., and Ang, H. M. (2010). Removal of emulsified oil from oily wastewater using agricultural waste barley straw. Biochemical Engineering Journal, 49 (1), 78-83.

Moazed, H., and Viraraghavan, T. (2005). Use of organo-clay/anthracite mixture in the separation of oil from oily waters. Energy sources, 27 (1-2), 101-112.

Sokolovic, J., Stanojlovic, R., Ciric, D., Jovanovic, G., Kirov, M., Stankovic, S., Gardic, V. (2013) 'Investigation of the possibility of application of oily wastewater from RTB Bor in the coal flotation', Proceedings of the 8th Symposium „Recycling Technologies nad Sustainable Development, Bor Lake, Bor, Serbia, 243

Notes on the authors

JOVICA SOKOLOVIĆ, RODOLJUB STANOJLOVIĆ: University of Belgrade, Technical faculty in Bor, Serbia

SUZANA STANKOVIĆ, VOJKA GARDIĆ: Mining and Metallurgy Institute, Bor, Serbia