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Wastewater treatment of emulsion bitumen plants by adsorption process

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Abstract

Although the emulsion bitumen plants produce little waste, they have been known as the green industry. The wastewater of these plants is transparent in appearance and because of having amine compounds, has foaming properties. Due to the use of sulfuric acid during the process, the pH of the produced wastewater is about 2. As a result, the biological treatment of wastewater becomes impossible. Chemical Oxygen Demand (COD) of the wastewater is about 20000 mg/lit indicating that its pollution load is very high. In the present study the potential of adsorption process for treating wastewater produced from emulsion bitumen plants was investigated. Adsorbents such as, sawdust, activated carbon, human hair, TiO₂ and nano-TiO₂ were studied. The results showed that the adsorption process can be used successfully in treating this type of wastewater. Sawdust as an adsorbent reduced 96% of pollution load at pH =10.

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Introduction

Adsorption process as a simple methods has very advantages in comparison to the other wastewater treatment technologies. Lower price, more convenient design, and more accessibility are the main advantages of this process. Various natural and synthetic adsorbents have been used in this process. However, the use of biocompatible compounds and natural wastes as low cost adsorbents with high absorption capacity, is growing rapidly. Adsorption is a two-phase mass transfer process in which pollutants from the liquid phase, optionally build on unsaturated solid surfaces, this will significantly reduce pollutant concentrations in the liquid phase. Adsorption is a thermodynamic system where different compounds are in competition to reach equilibrium (Parsons, 2004).

Adsorption process takes place under steady and transient state. The primary force affecting the adsorption process, are the electrostatic force of attraction and repulsion between adsorbate and adsorbent molecules, these effective forces can be physical or chemical. Recently, low-cost natural adsorbents with biodegradability such as human and agricultural wastes have been discussed largely. These materials are biocompatible and available in large quantities. The amount of a substance adsorbed on an adsorbent is a function of several factors. These factors include the amount and quality of surface area, temperature, concentration and the type of adsorbent. Important adsorbent in industry have surface area more than 1000 m²/g. This amount of surface area only possible if adsorbent has porous structure. Also the pore network have to be in a manner that all internal pores of adsorbent is accessible to the adsorb material (Parson, 2004; Jonidi *et al.*, 2009).

Today, many studies are done employing various natural materials as adsorbents, particularly waste produced by humans. Such materials can be act like activated carbon and are so cheaper than that. For example, Samarghand *et al.*, (2008) in their study investigate the use of sawdust Raji tree for remove the

Chromium from the environment. In their study they are investigate the effect of pH, contact time, amount of adsorbent and initial concentration of Cr(IV). Rahmani *et al.*, (2008) also compared the performance of three kinds of sawdust as low cost adsorbents for the removal of arsenic and cyanide from wastewater, in their study they succeed to remove 83% cyanide with poplar sawdust and 96% arsenic with sawdust Raji tree. Darvishi *et al.*, (2008) used biological sludge as an adsorbent and were able to absorb cadmium from wastewater. Samadi *et al.*, (2008) took advantages of bone coal to absorb fluoride from drinking water. They discovered that amount of fluoride removal in water, depending on the parameters of residence time, bone particle size and pH of solution. Eramiavval, (2008) in his study with help of activated carbon that produced it from coconut fiber, succeeds to attract the heavy metal nickel. In his research, it was found that the amount of adsorption is strongly dependent to pH and maximum of adsorption is take place at pH= 4.

Emulsion bitumen is achieved from a mixture of bitumen, water and an emulsifying agent. Amount of emulsifying agent is very low and about 0.3 to 0.5% by weight of bitumen (Hami, 2006). The amount of water consumption in this type of bitumen is about 30 to 50 weight percent of bitumen. Generally emulsifying agent is alkaline salts of organic acids or ammonium salt that could charge the bitumen particles. The bitumen particles repel each other due to inductive load and floating in water with particle diameter of hundredth to one-thousandth millimeter (Tabatabaei, 1997). Emulsion bitumen is used in cold asphalt in humid environments or it is used in insulation, in this case water will be added to it and its concentration has to reach to 65% (Eramiavval, 2008; Tabatabaei, 1997).

In this study, wastewater treatment of emulsion bitumen plants was investigated by adsorption process. According to studies no research has been done on wastewater treatment of emulsion bitumen plants and this study is preliminary research in this

field and certainly more research is needed and further study is necessary. Adsorbents used in this study are sawdust, human hair, activated carbon, nano titanium dioxide and titanium dioxide. These adsorbents have been used in different concentrations and optimal amount of each of them is identified. The results of the current study could be useful in treatment of wastewaters in industrial plants and effective in achieving environmental standards.

Materials and methods

Materials

The main chemicals used in this research are: sawdust, human hair, activated carbon, nano titanium dioxide and titanium dioxide and apparatus for measurement of COD. Sawdust that has been used is produced from pine tree and other chemicals are from Merck Company.

Equipment

The main instrument used in this research are: JENWAY 6305 Spectrophotometer, Joun-B3.11 Centrifuges, HANNA PH211 pH, COD meter, Jar test model ZAG SHIMI and Ultrasonic bath model DSA100-SK2-4.0L.

Procedure

For adsorption experiments, in first step the adsorbent particles of sawdust, activated carbon and human hair are aggregated by laboratory sieve and particles between 20 and 40 mesh were used for adsorption experiments. Nano titanium dioxide and titanium dioxide adsorbent were used without any modification or aggregation. Then, different amount of adsorbent was added to a certain volume of wastewater samples and was stirred by magnetic stirrer for 10 minutes in order to complete the mixing process. Then the mixture filtered using filter paper No.2 and the COD of the solution was measured.

Results and discussion

Effect of adsorbent dose on COD removal rate

Sawdust is a cheap and abundant material that usually used as an adsorbent to remove contaminants

from water. Chemicals such as paint, oil, toxic salts and heavy metals can be removed effectively by organic materials. This study used Russian pine sawdust for removing these contaminants. Sawdust is one of low cost and reliable adsorbent for removal of pollutant from wastewater. Sawdust is available and efficient adsorbent that effective in removal of numerous contaminants such as paint, oil, salts, heavy metals and etc. Many agricultural products such as sawdust are available in large quantities in lumber mills could be used in this process. Using sawdust for removal of contaminants could eliminate large amount of COD.

The results of experiments showed that with increasing adsorbent from 16 to 24 grams per liter, the removal rate of COD is increased, however this increase is minimal. As can be seen in Fig.1, 16 g/L of sawdust adsorbent have a good performance in respect to the economic issues and test development so the amount of 16 grams per liter is considered as optimal.

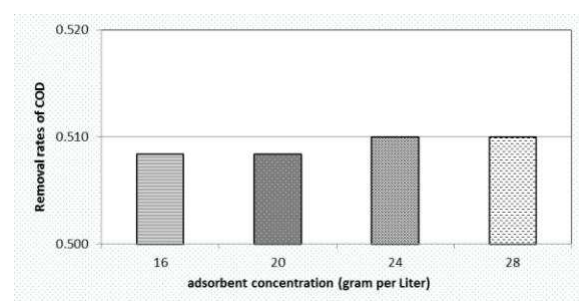


Fig. 1. Effect of the adsorbent concentration (sawdust) on COD removal of wastewater.

Humai hair can be used as an effective adsorbent for the removal of pollutants from wastewater. Fig.2 shows the effect of adsorbent dose on the COD removal rate. As shown in Fig.2, with the increasing amount of adsorbent from 16 to 24 g/L, removal of COD were not significantly increased. But with the increasing amount of adsorbent and reaching the limit of 28 g/L, adsorption has increased considerably. However the increase over this amount does not lead to increased significantly in adsorption efficiency and enhancement in respect to adsorption

was low. Therefore, the amount of 16 g/L of the adsorbent was selected as the optimum value.

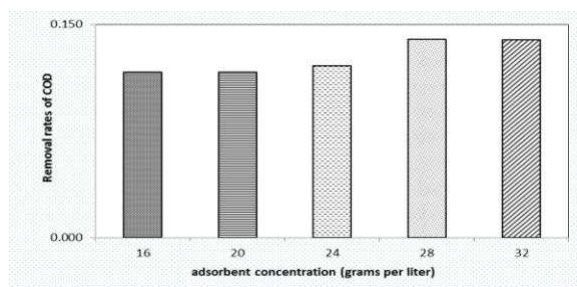


Fig. 2. Effect of the adsorbent concentration (human hair) on COD removal of wastewater.

The need for higher quality wastewater treatment was lead to deep and extensive study of the adsorption process on activated carbon. Wastewater treatment with activated carbon usually considered as a final cleaning process that applied to water that exposed to conventional biological treatment. In this case, carbon is used for separation of the remaining dissolved organic materials. Depending on apparatus that contact carbon with water, it also could separate the fine solids. Granular carbon can easily be recovered with oxidation of organic materials in oven and remove them from carbon surface. The results of experiments are shown in Fig.3. As is evident with increasing adsorbent quantity from 5 to 40 g/L, COD removal rates increases. This increase with respect to the amount of adsorption is very small and could not be economically affordable. Therefore, According to the bar graphs in Fig.3, and economic considerations, the amount of 5 g/L adsorbent was selected as the optimum value.

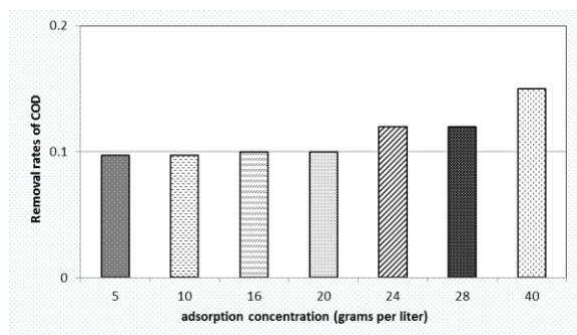


Fig. 3. Effect of the adsorbent concentration (activated carbon) on COD removal of wastewater.

Comparison between sawdust, human hair and activated carbon adsorbents and consideration of economic costs, sawdust shown better performance than other adsorbents. This Comparison is shown on Fig.4. The wastewaters COD removal by 16 g/L sawdust, function more effective than a human hair and activated carbon adsorbents. Therefore, in respect to presence of sawdust in wastewater and economic costs, use of this adsorbent is more effective than others.

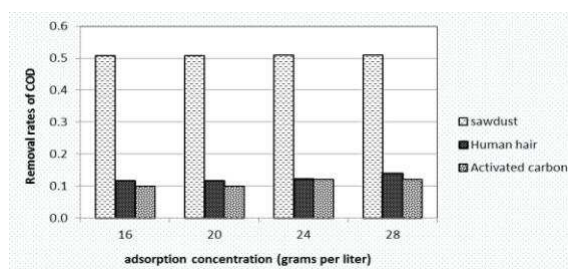


Fig. 4. Comparison of different adsorbents (sawdust, human hair and activated carbon) on COD removal of wastewater.

Titanium dioxide is one of metal oxides that widely used in daily life, this substance is white powder that contain Anatase, Rutile and Brookite crystalline phases. The powder of this material used as a white pigment in industry. Band gap of this material is about 2.3 electron volts (Anatase type) that can absorb ultraviolet light. This property can be used as UV absorbers in sunscreen usage. The comparison of nano titanium dioxide and titanium dioxide adsorbents capacity are shown in Fig.5. As can be seen, 0.8 g/L of nano titanium dioxide is optimal for COD removal rate.

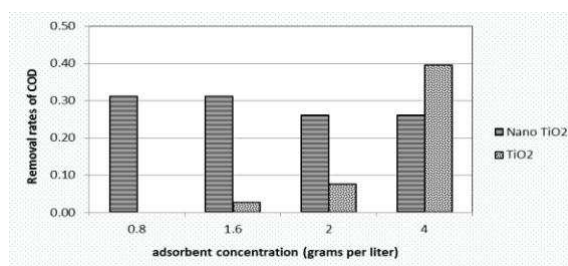


Fig. 5. Comparison of different adsorbents (nano titanium dioxide and titanium dioxide) on COD removal of wastewater.

Effect of pH

To investigate the effect of pH on the efficiency of process, we will change the pH of wastewater to 5, 7 and 10. Then 16, 20, 24 and 28 g/L of adsorbent (sawdust, human hair and activated carbon) were added to the solution. As can be seen in Fig. 6, COD removal rate in pH=10 for sawdust is approximately 95%. This removal rate for titanium dioxide and nano titanium dioxide adsorbents was around 94%.

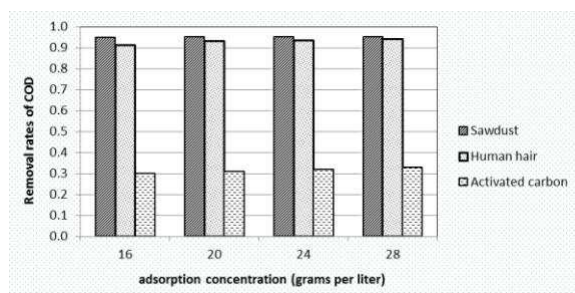


Fig. 6. Comparison of different adsorbent (sawdust, human hair and activated carbon) on COD removal of wastewater at pH=10.

The effect of pH on COD removal is shown in Fig.6. As is clear, at pH=10 sawdust in amount of 16 g/L has shown a better performance than other adsorbent. Also, the adsorption of pollution in optimal conditions was shown approximately 95%. Thus, the use of this adsorbent in alkaline conditions is more logical.

The effect of pH on COD removal rate is shown in Fig.7. As is clear, in pH=7 sawdust in the amount of 16 g/L shown a better performance than others. Also, the adsorption of pollution in optimal conditions was shown approximately 91%. Thus, the use of this adsorbent in Neutral solution is more logical.

Considering fig.s 6, 7 and 8 we discover that adsorption process take place effectively in alkaline condition rather than acidic condition and the sawdust has better performance than other adsorbents.

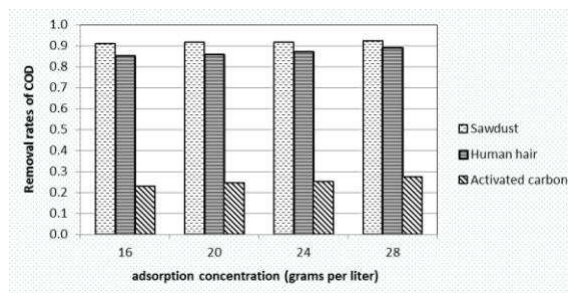


Fig. 7. Comparison of different adsorbent (sawdust, human hair and activated carbon) on COD removal of wastewater at pH=7.

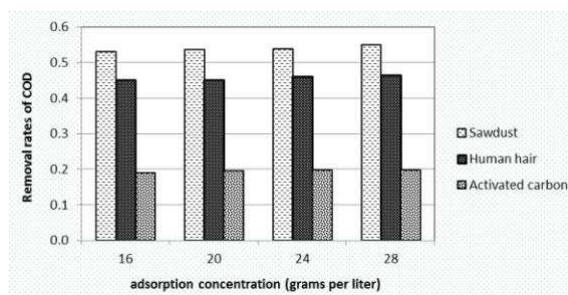


Fig. 8. Comparison of different adsorbent (sawdust, human hair and activated carbon) on COD removal of wastewater at pH=5.

The effect of pH on COD removal for titanium dioxide and nano titanium dioxide is shown in fig.s 9, 10 and 11. As can be seen, the alkaline condition has better performance on the removal rate. As can be seen, pH=10 was the optimum condition for the pollution removal. According to Fig.9, the COD removal efficiency in optimal conditions with 0.8 g/L adsorbent was about 90%.

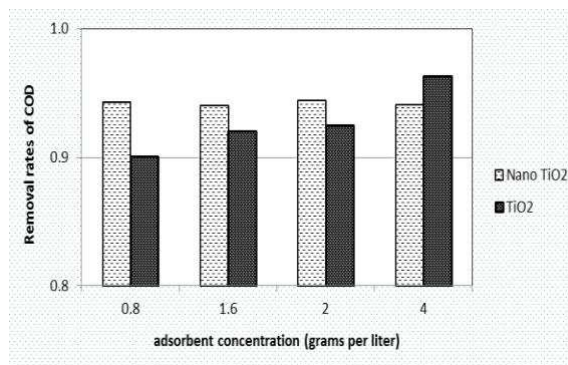


Fig. 9. Comparison of different adsorbent (nano titanium dioxide and titanium dioxide) on COD removal of wastewater at pH=10.

Considering the Fig.10, nano titanium dioxide showed better performance than titanium dioxide. As can be seen, the COD removal efficiency in optimal conditions with 0.8 g/L of adsorbent was about 91.5%.

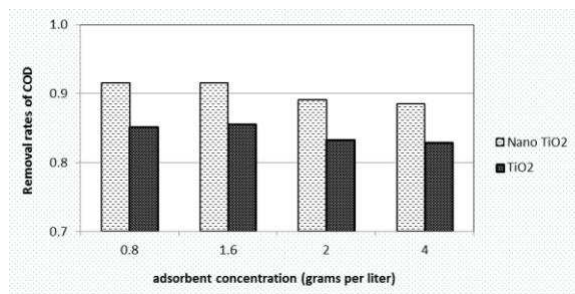


Fig. 10. Comparison of different adsorbent (nano titanium dioxide and titanium dioxide) on COD removal of wastewater at pH=7.

According to the above fig.s, it can be concluded that whenever we go from alkaline condition to the acidic one, we observe lower performance. As is shown in Fig.11, nano titanium dioxide adsorbent has better performance in removal of COD from wastewaters in alkaline conditions. According to Fig.11, the removal efficiency of COD in optimal conditions with 0.8 g/L of adsorbent was about 41%.

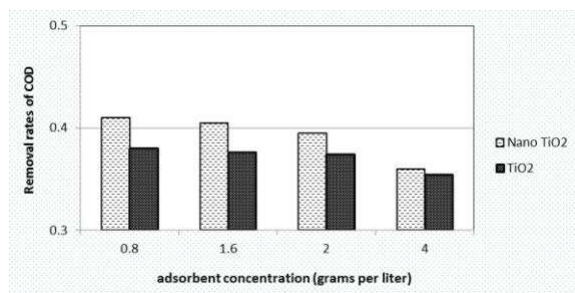


Fig. 11. Comparison of different adsorbent (nano titanium dioxide and titanium dioxide) on COD removal of wastewater at pH=5.

Effect of reaction time

To investigate the effect of reaction time on the process, reaction time of 10, 30, 45 and 60 minute were examined. Fig.12 shows the Changes in COD removal rate of the wastewater based on the reaction time. As shown in this fig., Since 10 to 45 minutes in

all adsorbents, the COD removal rate is ascending and after 45 minute, the slope is become very low therefore for the adsorption process the reaction time of 45 minute is appropriate and this time is considered as the optimal time for the process.

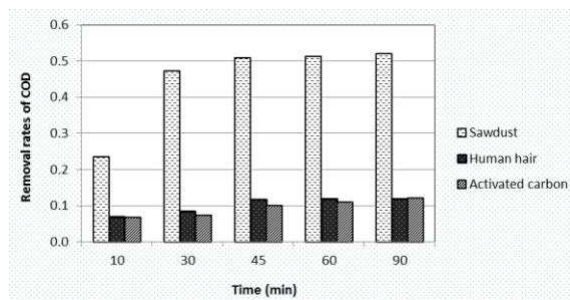


Fig. 12. Comparison of reaction time on the COD removal rate (C=0.1 g/l, pH=7).

Conclusions

In this study, wastewater treatment of emulsion bitumen plant has been studied by accessible and affordable adsorbent. According to the experimental results obtained, adsorbents used have shown better performance in alkaline conditions. After 45 minute, desirable pollution removal was achieved. Sawdust was able to eliminate 96% of wastewater pollution. It should be noted that nano titanium dioxide and titanium dioxide and human hair have done removal in the range of 94 to 95 percent. So it could be concluded that the adsorption process can be used for reduction of the wastewater pollution load of emulsion bitumen plants effectively. The results of this research could be used for future studies on treating this type of wastewater.

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