Journal of Pollution Effects & Control
Cui et al., J Pollut Eff Cont 2014, 2:2
DOI: 10.4172/2375-4397.1000122
Research Article Open Access

Oil-polluted Sea Water Purification by Carbonized Rice Hull

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Abstract

In recent years, marine oil pollution resulting from exploitation spills and accidents during oil transportation and use has affected the marine ecosystem safety, and oil polluted sea water remediation becomes a global problem. Rice hull possesses a good property of adsorption pollutants and it can be easily obtained from the abundant produce of rice all around the world. This experiment used carbonized rice hull (CRH) as adsorbent, aiming to purify oil polluted sea water and explore optimal adsorption conditions and effects. Six sets of experiments were done under the initial oil concentration of 1.35 mg/L and CRH dosages of 0, 6.67, 13.33, 20, 26.67, 33.33 g/L, separately. Seventy percent of oil was removed under the ideal dosage of 13.33 g/L, getting the minimum oil concentration of 0.39 mg/L. Another six sets of experiments were also done under the adsorption time of 0 h, 1 h, 2 h, 3 h, 4 h, 5 h and the same CRH dosage of 13.33 mg/L. The ideal removals of COD (35.5%) and oil (71%) were obtained after 3 hours adsorption, while the highest COD removal gets to 47.5%.

Keywords: Adsorption; Carbonized rice hull; Marine oil pollution; Oil polluted sea water

Introduction

In the latest decades, oil industry has developed so fast that it has become a crucial part of the world. However, oil pollution was among the major components of ocean pollution [1], oil and petroleum products that spilled into the ocean through various channels make 0.6% of annual oil productivity around the worlds. Leakage and blowouts during exploitation and natural spills at the undersea bottom are among the reasons that lead to marine oil pollution, which has become increasingly serious and called upon solving as the frequent occurrence of tanker accidents and drilling spills [2].

China is the largest developing country and has a huge quantity of oil production and consumption in the world. However, the problem of oil pollution is even more serious due to the lagging productive conditions and environmental technology and low public awareness of environment protection. Of the harm of marine oil pollution, there is not room to fully speak. It affects the growth of marine life, reduces the use value of coastline areas, damages coastal infrastructure and even destructs the self-purification ability of the ocean, thus destroying the marine ecosystem [3].

It is an urgent task to control and manage marine oil pollution efficiently. Some general methods are used for oil polluted sea water treatment as follows [4,5]: Physical methods including fence treatment, skimmers and oil adsorption materials such as straw, sawdust, etc; Chemical methods including dispersing agent, oil condensation agent and other chemical products; New treatment methods such as bio-remediation technology and combustion method, etc.

Marine pollution may get more seriously since the reagents from chemical methods are potential sources of secondary pollution. Only oil film on the sea surface can be removed by adsorption felt, while the removal effects of dissolved and emulsion oil are not so ideal, and the material cost is higher. Bacteria used in bio-remediation require carrier, it is impossible to keep better effect when used in a large area.

Many researches have been done works deeply in the field of preparation and adsorption performance of carbonized rice hull (CRH). Acid-treated rice hull was used as raw material by Junqing Qian to investigate the activation process of rice hull adsorbent, which presents evident adsorption effects to polycyclic aromatic hydrocarbons (PAHs) and heterocyclic dyes in water [3]. Rice hull adsorbent was also used by Malik to treat acid dye wastewater and the optimal adsorption conditions were confirmed, furthermore, its adsorption isotherms meet Languir and Freundlich equations [6].

The open-air firing CRH was used as adsorbent in this experiment in order to find effective methods to clean up oil residuals off the contaminated coast and purify oil-polluted sea water.

Materials and Methods

Rice hull is obtained from Liaoyang City, Liaoning province, China. The main physical and chemical indicators are as follows:

SiO_2%: ≤ 50; C%: ≥ 40; Ash%: ≤ 45; Bulk density g/cm^3: 0.1-0.3; Thermal Conductivity: ≤ 0.05; H_2O%: ≤ 3

The shape of CRH is shown in Figure 1.

Figure 1: Carbonized rice hull.

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Received September 22, 2014; **Accepted** October 29, 2014; **Published** November 10, 2014

Citation: Cui Y, Li J, Zhang Y, Zhang M (2014) Oil-polluted Sea Water Purification by Carbonized Rice Hull. J Pollut Eff Cont 2: 122. doi: 10.4172/2375-4397.1000122

Experiment plans are listed as follows:

- Prepare six mixtures of oil polluted sea water (750 ml, pH 6.83) and different quantity of CRH (0, 5, 10, 15, 20, 25 g) were in Erlenmeyer flasks (1000 ml), and absorb statically at room temperature for 3 days, then filter through the glass sand core funnel G4 (0.45 micron) and measure the oil concentrations.
- Prepare five mixtures of oil polluted sea water (750 ml) and CRH (10 g) in Erlenmeyer flasks (1000 ml), and absorb statically for 0 h, 1 h, 3 h, 5 h, 7 h, respectively, then filter through the glass core funnel G4 (0.45 micron) and measure the oil concentrations.
- Prepare five mixtures of oil polluted sea water (750 ml) and CRH (10 g) in Erlenmeyer flasks (1000 ml), absorb statically for 0 h, 1 h, 3 h, 5 h, 7 h, respectively, then filter through the glass sand core funnel G4 (0.45 micron) and measure the COD concentrations.

Three replicates were analyzed for each sample. Oil and COD concentrations were measured with UV spectrophotometry and alkaline potassium permanganate (The specification for marine monitoring (GB 17378.4-2007) in China), respectively.

Results and Discussion

The optimal adsorbent dosage

Six mixtures of sea water (750 ml) and CRH (various quantity of 0, 5, 10, 15, 20 and 25 g) were prepared, corresponding to CRH dosages of 0.00, 6.67, 13.33, 20.00, 26.67, 33.33 g/L, the results of oil concentration after adsorption were presented in Figure 2. The initial oil concentration of sea water was 1.35 mg/L. As shown in Figure 2, the oil concentrations decrease rapidly under the CRH dosages of less 13.33 g/L, getting the lowest concentration of 0.39 mg/L. However, no obvious oil concentration decrease occurs as the CRH dosages increase further, the lowest oil concentration is 0.22 mg/L under the experimental conditions.

From the point of oil removal efficiency, when the dosages of CRH range from 0 to 13.33 mg/L, the oil removals increase from 0 to 71%, while the dosages of CRH increases from 13.33 to 33.33 mg/L, the oil removals only improve 12.7 percentages, getting the highest removal of 83.7%. Thus, from economic viewpoint, the CRH dosage of 13.33 mg/L is the optimal choice.

The optimal adsorption time

The adsorption curves of different adsorption time under the same CRH dosage of 13.33 mg/L are presented in Figure 3, which show us the oil concentration variation in oil polluted sea water with time under the CRH adsorption. The oil concentrations decrease notably during initial time goes and tends to balance after a certain time. It is analyzed that the phenomena is related to the adsorption activity and surface structure of CRH adsorbent. Silicon containing in the rice hull plays the key role of adsorption. Silicon in the rice hull forms a spatial grid structure and exists in the interior of honeycomb holes which on the rice hull surface. At the beginning, adsorbate in the honeycomb holes is adsorbed rapidly, and corresponding to the higher removal efficiency. Then it becomes difficult for the adsorbent to be translated from the solution to adsorption activity sites due to the effect of micro-capillary. Consequently, desorption becomes dominant process. The adsorption tends to the balance after the micro-capillary effect is overcome.

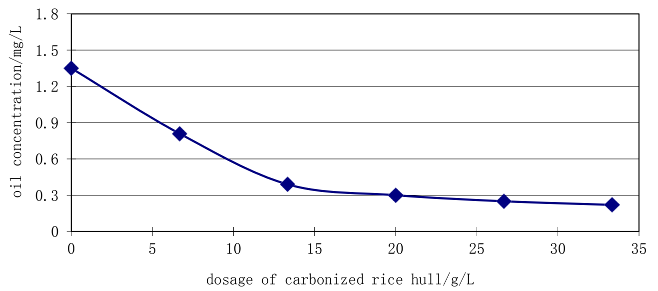

Figure 2: Oil concentration profile.

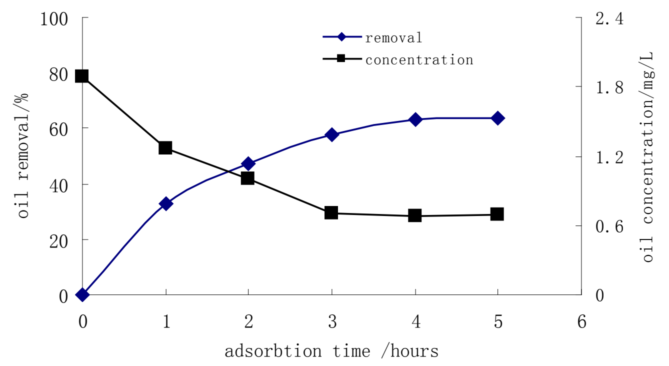

Figure 3: Curves of oil concentration with adsorption time.

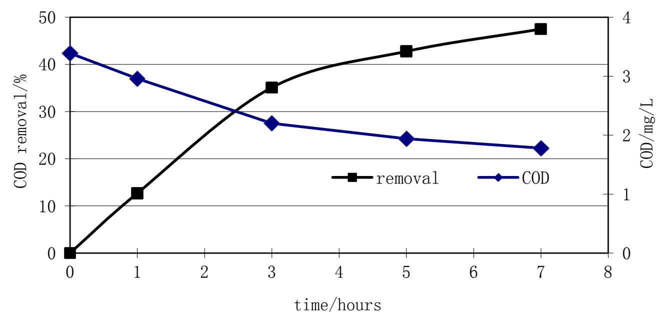

Figure 4: COD concentration and removal with adsorption time.

Adsorption efficiency increases rapidly in the first hour and tends to stabilization after three hours adsorption, the maximum oil removal is 71%. No obvious oil removal increase occurred after three hours, on the contrary, a little oil concentration increase appeared because of desorption process. As a result, the optimal adsorption time of CRH is three hours.

The removal of COD

Curves of COD removal efficiency and concentration with adsorption time are presented in Figure 4. Based on the experimental results, COD concentration decrease from 3.39 mg/L to 2.2 mg/L in the initial 3 hours adsorption, corresponding 35.1% of removal efficiency. Then it tends to stabilization, getting the lowest value of 1.78 mg/L and highest removal efficiency of 47.5%.

Combined Figure 3 and Figure 4, we found certain correlations between the removals of oil and COD in oil polluted sea water, which represent that the open-air firing CRH has strong adsorption ability in oil polluted sea water treatment.

The adsorption ability of CRH mainly depends on its physical and chemical structure on the surface. CRH is typically a kind of micro-porous carbon, which builds up a unique adsorption structure with a large number of unsaturated carbons on its surface [7]. It has high specific surface area containing lots of irregular structure or surface functional structure, thus producing a strong molecular field due to the relative function of micro-porous and porous wall molecular, providing a high-pressure system to physical and chemical changes of molecular in adsorption. Adjacent adsorption fields overlay under the role of Van Waals force when the micro-porous and molecular have the similar size, causing an increase in adsorption potential within the pore. As the surface of activated carbon fiber is covered with numerous porous and easily for adsorption and desorption, CRH is a kind of excellent adsorbent [8].

Conclusions

It is still blank in the purification of oil-polluted water by CRH adsorption. The experiment studied the optimal adsorption conditions and got following conclusions:

- CRH shows excellent adsorption ability to oil polluted sea water, by which soluble and emulsion oil in the sea water can be removed effectively.

- Different dosage of CRH represents different removal efficiency, the optimal adsorption time was 3 to 5 hours, the removal efficiency can get up to 71%.

In a word, CRH made from cost-effective rice hull shows ideal effects in the purification of oil-polluted sea water. As its producing process is simple and has an abundant resource of raw material, and the operation has the advantages of simple and low cost, thus this provides a bright road for rice hull deeply processing and utilization, besides, inspirational prospects can be seen in the treatments of oil-polluted sea water and sewage.

Acknowledgment

The research was financed by the Funds for the Scientific Research Fund of Public Welfare Undertakings, Liaoning Province (2014004006) and the Fundamental Research Funds for the Central Universities in China (DC12010205 and DC13010323).

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