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**REMOVAL OF SULFOLANE FROM WATER USING ACTIVATED CARBON ADSORPTION**

Yiqiao, Yang1, Linlong, Yu2,6, Sobhan, Iranmanesh3, Ian, Keir4, and Gopal, Achari5

1 Department of Civil Engineering, University of Calgary, Canada

2 Department of Civil Engineering, University of Calgary, Canada

3 Department of Civil Engineering, University of Calgary, Canada

4 Bonavista Energy Corporation, University of Calgary, Canada

5 Department of Civil Engineering, University of Calgary, Canada

6 [corresponding\_author\_linyu@u](mailto:corresponding_author_linyu@u)calgary.ca

**Abstract:** The objective of this research is to determine the effectiveness of two commercially available activated carbons to remove sulfolane from aqueous media. Batch adsorption experiments were conducted to determine each activated carbon’s maximum sulfolane adsorption capacity. The activated carbon demonstrating the highest sulfolane adsorption capacity was selected for further investigation, where the impact of pH, temperature, water quality and diethanolamine (DIPA) on sulfolane adsorption capacity was investigated. In addition, a regenerative method based on UV/H2O2 was developed to treat and recycle the exhausted activated carbons. The results showed the coconut shell based activated carbon performed better than coal based activated carbon. It was also found that the adsorption capacity was significantly impacted by DIPA being present in the water matrix. The regeneration study revealed the UV/H2O2 process can be successfully employed to regenerate the exhausted activated carbon by degrading the sulfolane desorbed from activated carbon.

# **INTRODUCTION**

Activated carbon adsorption is a well-known physical separation method featured by the accumulation of contaminants onto the surface of activated carbon. It is widely used in water and wastewater treatment processes to remove organic matters (Marsh et al 2006). In past several decades, the activated carbon adsorption has been successfully employed to remove industrial contaminants including dyes, surfactants, perfluorinated compounds, phenolic compounds and others (Karabacakoğlu et al. 2008, Al-Degs et al. 2008, Wu and Pendleton 2001, Hansen et al. 2010). Activated carbon’s adsorption capacity depends on multiple factors including temperature, type of contaminants, surface properties, solution ionic strength and pH. The activated carbon adsorption process can be driven by electrostatic or non-electrostatic interactions (Moreno-Castilla 2004). Electrostatic interaction takes place when adsorbate is an electrolyte and in dissociated or protonated form. The charged adsorbate and carbon surface develop attractive and repulsive forces, which controls the overall adsorption performance. Conversely, non-electrostatic interactions between activated carbon and adsorbate involve van der Waals force of attraction, hydrogen bonding and hydrophobic interactions (Moreno-Castilla 2004).

Activated carbons are produced from carbonaceous materials such as coal, lignite, wood, peat, nut shell and coconut shell (Cecen et al. 2011). Activated carbon derived from different raw materials usually differ in pore structure and surface area distribution. It is also available in different particle sizes and classified as granular activated carbon (GAC) or powdered activated carbon (PAC). GAC has diameter between 1.2 mm to 1.6 mm, is commonly used in continuous water treatment process and is easy to regenerate. In contrast, PAC has finer particle size with diameter less than 0.1 mm. The PAC exhibits a faster adsorption kinetics but hard to regenerate, leading to high operation cost.

In this study, GACs were investigated to treat an emerging industrial contaminant, sulfolane, from contaminated water. Sulfolane is an organosulfur compound mainly used to extract aromatics from hydrocarbon mixtures and sweeten sour gas in the Sulfinol® process. It has been frequently detected in the soil and groundwater near refineries and gas plants in North America. With a high water mobility, sulfolane can pose risk for off-site contamination.

So far, the study on sulfolane removal by using activated carbon adsorption is very limited and there is only one publication (Coggeshall and Price 2013) evaluated the feasibility of adopting activated carbon adsorption to remove sulfolane from aqueous media. In this research, the removal of sulfolane under various experimental conditions using activated carbon adsorption is investigated. Two commercially available activated carbons prepared from coal and coconut shell were selected as adsorbents. In addition, the impact of temperature, pH, water quality and diethanolamine (DIPA) on the performance of activated carbon adsorption is determined. Furthermore, a UV/H2O2 based method is developed to regenerate the exhausted activated carbons.

# **METHODS AND MATERIALS**

## **Materials**

Sulfolane with 99% purity, sodium hydroxide with 98% purity, hydrogen peroxide (ACS grade, ~30%), hydrochloride (ACS grade, ~37%) and diethanolamine (DIPA) with 99% purity were obtained from Sigma Aldrich, Canada. Sodium bicarbonate with 99% purity was purchased from VWR. Ultrapure water was used to prepare all chemical solutions. Groundwater samples were collected from sulfolane contaminated site. Two GACs derived from coal (Type A) and coconut shell (Type B) were obtained from confidential sources. The characteristics of activated carbons are presented in Table 1.

Table 1. Physical Properties for Type A and Type B activated carbon

|  |  |  |
| --- | --- | --- |
| Physical Properties | Type of activated carbon | |
| A | B |
| Raw Material | Coal | Coconut Shell |
| Iodine Number (mg/g) | 900 | 1100 |
| BET surface area (m2/g) | 660.3 | 895.2 |
| Total Pore Volume (cm3/g) | 0.407 | 0.483 |

## **Batch equilibrium adsorption study**

Different amount of GACs (20 mg ~ 400 mg) were added into 20 ml solution containing 100 ppm sulfolane. All samples were then tightly sealed and shaken vigorously for 24 hours at room temperature. After shaking, activated carbons were separated from water samples using a no. 80 mesh (180 μm) prior to the extraction. The amount of sulfolane adsorbed by activated carbon at equilibrium, qe (mg/g), was determined by Equation [1]:

[1] qe=(C0-Ce)V/W

where C0 and Ce (mg/L) are initial and equilibrium sulfolane concentration in the water, V (L) is the volume of solution and W (g) is the mass of dry activated carbon.

## **Interference study**

For interference study, 20 ml of solution containing 100 ppm sulfolane were mixed with 0.05 g activated carbon for one hour under different experimental conditions. The sulfolane concentration in the bulk solution before and after adsorption experiments were determined. Three pH levels (4, 7 and 10) and two temperature levels (6 oC and 22 oC) were investigated. pHs of solution were adjusted by using hydrochloric acid and sodium hydroxide, while the temperature was controlled by a fridge with digital temperature setting. Two types of water including groundwater and ultrapure water were used in this study. 100 ppm DIPA was also introduced into the solution to determine its impact on sulfolane adsorption by activated carbon.

## **Regeneration study**

0.3 g activated carbons were added into 100 ml solution containing 100 ppm sulfolane. The prepared sample was mixed vigorously by shaker for 1 hr to reach adsorption equilibrium. After adsorption, the activated carbon was separated from the solution using a no. 80 mesh. The activated carbons were then placed in a quartz beaker filled with 100 ml ultrapure water and exposed to UVC irradiation in presence of 3000 ppm H2O2 for 1.5 hours. The UVC irradiation is provided by a Luzchem photoreactor equipped with 10 UVC lamps. The light intensity measured in the quartz beaker was determined to be 5.3×1017 photon/s. Magnetic stirrer was used to enhance the contact between activated carbon and water. The regenerated activated carbons were then reused to adsorb sulfolane from water following the procedures outlined before. The sulfolane concentration in bulk solution and surface of activated carbon were analyzed to determine the effectiveness of regeneration.

## **Analytical procedure**

Liquid-liquid phase extraction procedure was used to extract sulfolane from the aqueous phase. Each 5 ml of water sample was extracted with 3 ml of dichloromethane (DCM). After extraction, 1 ml of DCM layer was transferred into GC vial using a pasturing pipette. The sulfolane concentration was then analyzed by Agilent 6890 gas chromatography (GC) equipped with auto-sampler and Flame Ionization Detector (FID). A fused silica capillary column (ZB 5MSI, Phenomenex) was used to separate sulfolane from other compounds. High purity helium was used as a carrier gas. The GC was operated on splitless mode with an injection volume of 1.0 µL. Temperature of injection port was held at 160 ˚C. The oven temperature was programmed as follows: initial temperature was set at 120 ˚C, then increased to 300 ˚C at a rate of 10 ˚C/min, the final temperature was maintained at 300 ˚C for 3 min. The FID temperature was held at 330 ˚C.

# **RESULTS AND DISCUSIONS**

## **Adsorption Isotherm**

The adsorption isotherms of sulfolane onto Type A (coal based) and Type B (coconut shell based) activated carbons are presented in Figure 1. The results showed that the adsorption isotherm for both activated carbons followed a concave curvature trend and are increased gradually. No definite plateau was observed with the investigated equilibrium sulfolane concentrations. It can also be seen from Figure 1 that Type B activated carbon adsorbed more sulfolane than Type A activated carbon for the same equilibrium sulfolane concentration in water. In order to quantitatively compare the adsorption capacity of two activated carbons, the experimental data were fitted into two classical isotherm models, namely Langmuir and Freundlich. The Langmuir isotherm model depicts monolayer adsorption process and suggest there is a limited number of adsorption sites available on adsorbent surface. Once an adsorbate adhered to a specific homogenous site, it assumes no further molecules can occupy that site (Allen et al. 2004). The linearized form of Langmuir isotherm can be represented as:

[2] Ce/qe=1/(Qmb)+Ce/Qm

where qe is the amount of solute adsorbed per weight of adsorbent (mg/g), Qm and b are the Langmuir constant represents the adsorption capacity and energy, and Ce is the equilibrium solution concentration of solute (mg/L).

The Freundlich isotherm model describes a multilayer non-ideal adsorption process and assumes heterogeneous surface energies (Karri et al. 2017), in which the adsorption activation energy is dependent on surface coverage. The linearized form of Freundlich isotherm can be expressed as:

[3] log(qe)=log(K)+1/n[log(Ce)]

where K and n are the Freundlich constants represents adsorption strength and intensity. Other terms are as defined previously.

Table 2 summarizes the Langmuir and Freundlich constants along with the coefficient of determination (R2) for Type A and Type B activated carbon. It was calculated both R2 are greater than 0.9, indicating the adsorption process of sulfolane can be adequately described by both Langmuir and Freundlich model. Comparing the model parameters, Type B activated carbon has a higher adsorption capacity (Qm=28.82 mg/g) and considerable adsorption strength (K=5.33). The higher adsorption capacity of Type B activated carbon can be explained by its better surface properties. As shown in Table 1, coconut shell based Type B activated carbon has a larger iodine number (1100 mg/g), BET surface area (895.2 m2/g) and total pore volume (0.48 cm3/g) than Type A activated carbon. As reported by Hashimoto et al. (1975), activated carbon derived from coconut shell had a larger ratio of micropores (higher surface area), whereas coal based activated carbon had a macroporous structure (lower surface area).

Figure 1. Adsorption isotherm of sulfolane onto Type A and Type B activated carbon

Table 2. Fitting parameters of Langmuir and Freundlich models for Type A and Type B activated carbon

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Langmuir Equation | | |  | Freundlich Equation | | |
|  | Qm | b | R2 |  | K | n | R2 |
| Type A | 21.79 | 0.10 | 0.931 |  | 3.63 | 2.55 | 0.984 |
| Type B | 28.82 | 0.18 | 0.962 |  | 5.33 | 2.56 | 0.991 |

## **Adsorption Interferences**

Type B activated carbon (coconut shell based) was selected for further optimization study due to its high sulfolane adsorption capacity. The optimization study investigated the impact of pH, temperature, water quality and DIPA on sulfolane adsorption by activated carbon. The degree of impact was assessed by comparing the sulfolane removal percentage under different conditions with the control experiments and the result is summarized in Table 3. It is observed that pH had a negligible influence on sulfolane adsorption, whereas, the temperature, water quality, presence of DIPA have relatively higher impact. Less than 1% variations between pH adjusted samples and control samples shows a possible non-electrostatic interaction between sulfolane and activated carbon. Lower temperature (6 °C) benefited the activated carbon adsorption by a 7.8% increase on sulfolane removal, which can be attributed to the decreased sulfolane solubility as temperature decreased (Tan et al. 2008). The reduced solubility indicates a weakened bonding force between sulfolane and water, leading to more sulfolane to be adsorbed by activated carbon. The sulfolane removal through activated carbon adsorption in the groundwater was 7.1 % lower than ultrapure water; presence of DIPA reduced the sulfolane removal percentage by 25.8%. All of these impacts are caused by competition of different interferences for the available adsorption sites on the activated carbon surface (Worch 2012, Matsui et al. 2003). The humic matters in the groundwater samples can possibly compete with sulfolane for activated carbon’s available adsorption sites and inhibit the sulfolane removal rate. Zeinali and Najafpour (2010) reported that DIPA can be effectively removed from water by using activated carbon, indicating that DIPA occupies the activated carbon’s adsorption sites and reduces sulfolane adsorption capacity.

Table 3. The impact of pH, temperature, groundwater and DIPA on percent sulfolane removal

|  |  |  |  |
| --- | --- | --- | --- |
| Sample No. | Experimental condition\* | | Variation from control  (%) |
| Control | pH: 7  Ultrapure water matrix | Temperature: 22 °C  DIPA Conc.: 0 ppm | ± 0.00 |
| A1 | pH: 4 | | + 0.67 |
| A2 | pH: 10 | | - 0.83 |
| B1 | Temperature: 6 °C | | + 7.80 |
| C1 | Groundwater matrix | | - 7.10 |
| D1 | DIPA Conc.: 100 ppm | | - 25.80 |

\*The parameter listed is the only experimental condition changed compared to control experiment.

## **Feasibility Study of Using UV/H2O2 to Regenerate Exhausted Activated Carbon**

The regeneration method used in this study follows a two-step process, where sulfolane is firstly desorbed from activated carbon in ultrapure water and furtherly degraded by UV/H2O2 treatment. Table 4 presents the amount of sulfolane on activated carbon before and after UV/H2O2 treatment. It is observed the amount of sulfolane on activated carbon decreased from 4.32 mg to 2.46 mg after 1.5 hours UV/H2O2 treatment, indicating the two-step process can remove and degrade the sulfolane adsorbed onto activated carbon, and release the number of active adsorption sites. Yu et al. (2016) reported that more than 99% of sulfolane can be degraded after 30 minutes of exposure to UV/H2O2 system. However, the sulfolane removal rate (44% in 1.5 hours) in our study is considerably low. This can be explained by the following two possible mechanisms: (a) the overall sulfolane removal rate from activated carbon is governed by both desorption process and UV/H2O2 degradation. Sulfolane desorption process is relatively slower than UV/H2O2 degradation, leading to a lower overall degradation rate; (b) The presence of activated carbon in the water can significantly reduce the UV transmission and result in an inefficient photon utilization. The results show that a 1.5 hour regeneration can only partially remove sulfolane from activated carbon. It is expected that a longer treatment period can completely desorb and degrade sulfolane from exhausted activated carbon.

Table 4. Amount of sulfolane on activated carbon before and after 1.5 hours UV/H2O2 treatment

|  |  |  |
| --- | --- | --- |
| Adsorption Stage | Sulfolane on activated carbon (mg) | Sulfolane in water  (mg) |
| Before UV/H2O2 treatment | 4.32 | 0 |
| After UV/H2O2 treatment | 2.46 | 0 |

The sulfolane adsorption performance after multiple adsorption-regeneration cycles was investigated and the results were summarized in Table 5. It is observed that the regenerated activated carbon can be reused to adsorb sulfolane from water. Initially, the fresh activated carbon can remove 21.6 mg/g sulfolane from water. After one, two, three and four adsorption-regeneration cycles, the amount of sulfolane adsorbed by the activated carbon are 14.27 mg/g, 11.43 mg/g, 12.23 mg/g and 11.30 mg/g, respectively. The decreased sulfolane removal after regeneration can be explained by the reduced available adsorption sites resulted by the incomplete regeneration. It is hypothesized that completely regenerated activated carbon (longer UV/H2O2 exposure) can obtain similar sulfolane adsorption as fresh activated carbon. As shown in Table 5, the amount of sulfolane adsorbed on activated carbon was not significantly changed after four adsorption-regeneration cycles, indicating that UV/H2O2 treatment did not alter the treated activated carbon’s surface chemistry and pore structure. The total amount of sulfolane removed from water by using activated carbon adsorption increased with the number of adsorption-regeneration cycles. The cumulative mass of sulfolane removed from water through four adsorption-regeneration cycles achieved 21.25 mg, which is three times greater than the mass of sulfolane removed by the fresh activated carbon, indicating that the four cycles regeneration can reduce 70% of activated carbon usage.

Table 5. Adsorption performance after consecutive batch adsorption cycles

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Regeneration Cycle | Mass of sulfolane removed from water (mg/g) | Total amount of sulfolane adsorbed on activated carbon (mg/g)\* | Cumulative mass of sulfolane removed from water  (mg) | |
| 0 (Fresh) | 21.60 | 21.60 | | 6.48 |
| 1 | 14.27 | - | | 10.76 |
| 2 | 11.43 | - | | 14.19 |
| 3 | 12.23 | - | | 17.86 |
| 4 | 11.30 | 21.80 | | 21.25 |

\*The total amount of sulfolane adsorbed includes the previously unremoved and newly adsorbed sulfolane mass.

# **CONCLUSION**

In this study, activated carbon was shown to be a promising adsorbent to remove sulfolane from contaminated water. Specific conclusions were summarized as below:

* Coconut shell based activated carbon achieve a better sulfolane adsorption performance than coal based activated carbon.
* pH did not impact the sulfolane adsorption efficiency.
* Presence of DIPA can decrease the sulfolane adsorption on activated carbon.
* UV/H2O2 process can be used to regenerate exhausted activated carbon.
* Multiple adsorption-regeneration cycles can reduce the usage of activated carbon.

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# **REFERENCES**

Al-Degs, Y. S., El-Barghouthi, M. I., El-Sheikh, A. H., and Walker, G. M. 2008. Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and pigments*, **77**(1), 16-23.

Allen, S. J., Mckay, G., and Porter, J. F. 2004. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of colloid and interface science*, **280**(2), 322-333.

Coggeshall, M., and Price, S. 2013. U.S. Patent Application No. 13/196,697.

Hansen, M. C., Børresen, M. H., Schlabach, M., and Cornelissen, G. 2010. Sorption of perfluorinated compounds from contaminated water to activated carbon. Journal of Soils and Sediments, **10**(2), 179-185.

Hashimoto, K., Miura, K., Yoshikawa, F., and Imai, I. 1979. Change in pore structure of carbonaceous materials during activation and adsorption performance of activated carbon. Industrial & Engineering Chemistry Process Design and Development, **18**(1), 72-80.

Karabacakoğlu, B., Tümsek, F., Demiral, H., and Demiral, İ. 2008. Liquid phase adsorption of phenol by activated carbon derived from hazelnut bagasse. J. Int. Environmental Application & Science, **3**(5), 373-380.

Karri, R. R., Jayakumar, N. S., and Sahu, J. N. 2017. Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon. *Journal of Molecular Liquids*, **231**, 249-262.

Marsh, H., Rodríguez-Reinoso, F., and ebrary, I. 2006. *Activated carbon*. 1st ed, Amsterdam: Elsevier.

Matsui, Y., Fukuda, Y., Inoue, T., and Matsushita, T. 2003. Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. Water Research, **37**(18), 4413-4424.

Moreno-Castilla, C. 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon, **42**(1), 83-94.

Tan, I. A. W., Ahmad, A. L., and Hameed, B. H. 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. Journal of hazardous materials, **154**(1-3), 337-346.

Worch, E. 2012. *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter.

Wu, S. H. and Pendleton, P. 2001. Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity. Journal of colloid and interface science, **243**(2), 306-315.

Yu, L., Mehrabani-Zeinabad, M., Achari, G., and Langford, C. H. 2016. Application of UV based advanced oxidation to treat sulfolane in an aqueous medium. Chemosphere, **160**, 155-161.

Zeinali, F., Ghoreyshi, A. A., and Najafpour, G. D. 2010. Adsorption of dichloromethane from aqueous phase using granular activated carbon: isotherm and breakthrough curve measurements. Middle-East J. Sci. Res., **5**(4), 191-198.