Synthesis and Characterization of Metal Oxides Mesoporous Monoliths for Water Remediation

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Abstract

In recent years, a large number of industrial oil spills and toxic impurities have become an enormous environmental hazard for coastal human inhabitants and oceanic ecosystem. Due to such events there has been much effort in the development of hydrogels and polymer based membranes capable of extracting such impurities from water, yet prone to be chemically and mechanically degradation. Metal oxide mesoporous monoliths are promising candidates to tolerate such harsh oceanic environments. The network of micropores and mesoporous can be modified to enhance hydrophilicity and oleophilicity by tuning the porosity and structure surface through the implementation of sol-gel synthesis methods. Our research focuses on generating earth abundant, stable and reusable metal oxide mesoporous monolith with the capabilities to selectively remove organic contaminants from surface of sea water. Experiments were conducted using HfO_2 and ZrO_2 mesoporous monoliths and implementing Sudan (III) dye as an indicator for various organics and its mixtures such as benzene, toluene, methanol and gasoline. Qualitative analysis of organic adsorption from HfO_2 and ZrO_2 at the surface of seawater was contacted using ultraviolet-visible spectroscopy. Preliminary results showed that HfO_2 on average adsorb 20 µL containing 218 ppm Sudan (III)/Benzene solution under 53.2 seconds and average weight percent increase of 67 % of HfO_2 mesoporous having a dry interval of 1 minute.

Further characterization will be implemented to quantify the removal of organics from solution. Hence, additional characterization techniques such as Nuclear Magnetic Resonance (NMR), and Infrared Spectroscopy (FTIR) will be used in future studies to further elucidate the extent of which as synthesized HfO_2 and ZrO_2 mesoporous monoliths to selectively tune the monolith surface chemical functionality towards the removal of such small organic molecules from surface of water.

Introduction

In 2010 the National Oceanic and Atmospheric Administration (NOAA) reported one of the largest oil spills in U.S history which was the explosion of Deepwater Horizon oil rig off the Gulf of Mexico. The oil spill covered 42 miles coastline of Louisiana and after three months of trying to cap the leak is was estimated that the 3.19 million barrels of crude oil was released to the environment.[1] When it comes to such disasters scientist have strived to develop materials that have the capacity of being able to remove such oil and other impurities from the surface of the water. The type of material being developed are porous membranes or composite materials capable of adsorbing and purify harmful impurities from water. Recent development of highly porous hydrogels and carbon/silicon polymer based membranes/foams have shown to have the capability such impurities from water. Highly porous and ultralow density 3D graphene foams and Graphene Oxide (GO) hydrogels/ aerogels have been shown to exhibit excellent absorbance for removing heavy metal ions and organic oils from water.[2] Though the surface of the hydrogels and aerogels can degrade when exposed to various pH levels while mechanical degradation allows such materials pose an issue when it comes to the reusability of such materials.[2] 3D graphene developed using scallop-based approach where acid was poured onto scallop shells resulting to porous CaO_2 substrate template has also shown to be a great materials for removing impurities from the surface of water.[3] Due the graphene's very hydrophobic nature, researchers have conducted an experiment on the performance of the adsorption capacity of organic impurity by tagging such organics impurities, petro oils and ethanol, with Sudan (III) and measured adsorption of the 3D graphene foam to be 200-250 times its dry weight while having a pore size of 300 nm. [3]

Reusability of mechanical extraction of organics of such hydrogels and carbon polymers-based foams are not robust systems and have shown to be deleterious behavior under highly acidic and alkaline environment.[2] Other type of materials that are highly porous which are able to retain mechanical integrity are metal oxide mesoporous monoliths such as ZrO_2 and HfO_2 have been studied to have similar porosity as such carbon-polymer foams allowing metal oxide mesoporous monolith suitable for adsorption of liquid organic contaminates. The bimodal pore structure of the metal oxide mesoporous monolith composed of interconnected network of micropores and mesoporous, when prepared through sol-gel synthesis uses polymer precursors to polymerize gelation of various compounds, we can develop selective variations of pore sizes that contributes to interactions of fluid and metal oxide monoliths surface.[4] Studies have shown that

ZrO_2 and HfO_2 mesoporous monoliths to have porosity 87.4 % and 78.4 % with an average pore diameter 277 nm and 394 nm, respectively, with a capacity to tolerate extreme acidic and alkaline environments due to chemical functional groups at the surface crystalline structure.[6] Sol-Gel synthesis method was implemented to construct scalable free standing metal oxide mesoporous monoliths and research have shown that when annealed at 700 °C HfO_2 and ZrO_2 develops a monoclinic configuration allowing HfO_2 and ZrO_2 to be rigid enough to be mechanically stable under harsh environments.[7] Three different activations site are known to be present on the surface metal coordination of HfO_2 and ZrO_2, Browsted acid, Browsted base, Lewis acid sites makes the monolith amphoteric meaning that the metal oxide mesoporous monolith when subject to a multitude of acidic/basic mediums the monolith would reach equilibrium relatively quickly at surface by simply changing to its pH to corresponding medium.[6] Our studied uses UV-Vis to analyze the adsorption of 33.3 PPM Sudan (III)/Gasoline solution and 45 PPM Sudan (III)/Benzene using HfO_2 mesoporous monolith annealed at 700℃ from the surface of water. Adsorption kinetics studies of 218 PPM Sudan (III)/Benzene demonstrated an average increase weight capacity of non-uniformed HfO_2 mesoporous monoliths after the adsorption of 20 μL and 30μL within a time frame of 53.2 seconds and 60.4 seconds respectfully. Preliminary results from this study will enable implementation for scalable and robust pores materials capable of selectively remove organic liquids from surface of water and potentially further extend contaminant removing harmful organic impurities such a crude oil from our oceans and rivers, making it a powerful tool towards restoring and cleaning oceanic ecosystems and communities from pollutant water.

Methods

Solid Zironium Tetracholride and Hafnium Tetracholride are initially hydrolyzes by adding H_2O to produce Zironyl cholride and hydrochloric acid gas. 24 hours later N-methylformamide (NMF) is added during the hydrolysis producing formic acid and methyl ammonium which increases the pH during hydrolysis. This leads to inducing production of more product depicted in reaction (1). NMF acts as a porogen affecting both phase separation during polymerization, surface porosity and pore size. After 2 days the addition of polyethylene oxide (PEO) which further induces phase separation and increasing the porosity of the monolith. Polyproylene oxide (PPO) is a proton scavenger as shown in reaction (3) it is added during the polycondensation then vortexed until polymerization/ gelation of metal oxide initiated in reaction (2)

$$MCI_4 + H_2O \rightarrow\ MOCI_4 \cdot H_2O + 2HCI \quad \textbf{(1)}$$

$$MOCI_2 \cdot 8H_2O \quad MO_2(gel) + HCI \quad \textbf{(2)}$$

$$C_3H_6O\ \boldsymbol{(PPO)} + HCI \rightarrow CIC_3H_6OH \quad \textbf{(3)}$$

Metal oxide gel is then placed in the furnace at 50 °C for three days. During this process the gel turns to a whole solid precipitate monolith during this stage the monolith is susceptible to cracks and fracture due to the capillary force from the surface tension of the liquid water retained after heating. Solvent exchange is implemented using (water, methanol, acetone, hexane, and pentane) in sequence by adding and removing each solvent within a time frame of 24 hours. The purpose of solvent exchange is to slowly introduce the monolith initiated from higher surface tension of polar solvent to lower tension nonpolar solvents. Solvent exchange also filters any leftover byproduct that is present after the polycondensation and polymerization of the metal oxide gel. The monolith is then annealed at certain temperatures and time period with a furnace ramp rate of 0.1 ℃/min see (Figure 1) the final product being annealed at 700℃ monoclinic crystal mesoporous metal oxide monolith.

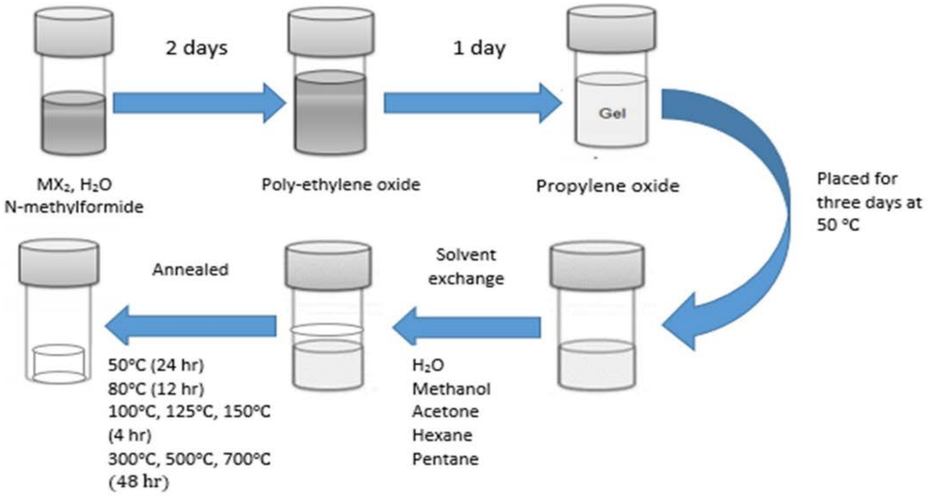

Figure 1. Experimental procedure to synthesis metal oxide monoliths via sol gel- process[1].

Adsorption Kinetics Method

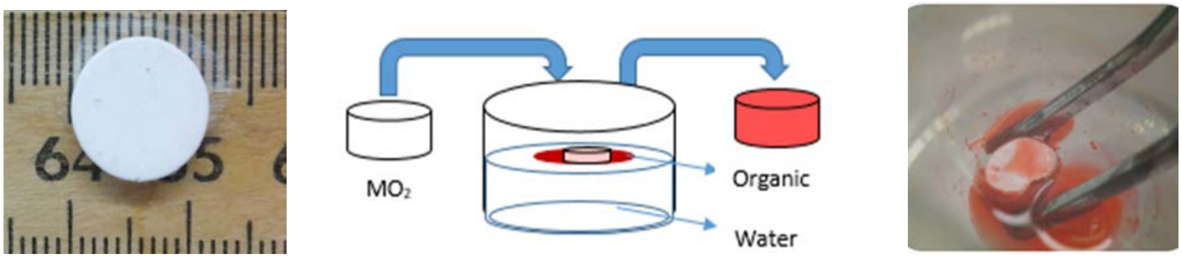

Figure 2: *Adsorption Diagram of Metal Oxide Mesoporous Monoliths with Dye/Organic on the surface of water*

Adsorption Kinetics Method is used to analyze the adsorption capacity (Q_f) and measures how long it would take in terms of second (s) of the metal oxide mesoporous monolith HfO_2 and ZrO_2 to completely adsorb the organic/dye solution from the surface of the water. The wet weight of monolith after 5 minutes of drying at room temperature (m_f). The initial dry weight of monolith(m_i).

$$Q_f = \frac{m_f - m_i}{m_i}.$$

We initially pretreat a 400 mL glass beaker by rinsing it with Rain-X and Methanol three times. This allows for the organic/dye solution not adhere to the surface of the glass wear. 200 mL of seawater were dispensed in the pretreated 400 mL beaker. Four types of organics were analyzed for adsorption during this experiment; 45 PPM Sudan(III)/Benzene, 33.3 PPM Sudan(III) /Gasoline, 30 PPM Sudan(III)/Methanol, 31.26 PPM Sudan(III)/Toluene solutions. Using a micropipette dispensed dye/organic solutions with corresponding measured volumes (20-300 μL) on the surface of the seawater and nano-water. The four samples of metal oxide mesoporous monolith were initially weighed and the duration of time(s) of each sample to partial or completely adsorb the various volume of dye/organic solutions on the surface of the seawater/nanopure water then recorded. A glass pipette was use to extract the surface liquid for further qualitatively analysis implementing Ultraviolet Spectroscopy Chromatography. The wet weight of the sample is then dried for 5 minutes then weigh and recorded. The reusability of the sample goes through a further drying period in a furnace at 50°C for an hour until the weight of the sample is ± 0.01 from its initial dry weight. This procedure is repeated for every distinct volume of dye/organic solution the sample is removing. The remaining liquid well be further analyzed utilizing Hydrogen Nuclear Magnetic Resonance (HNMR) as a qualitative approach to examine the type of the chemical compounds that are present within the liquid samples.

Results

Transmittance FTIR spectra analysis of HfO_2 and ZrO_2 mesoporous monoliths annealed at 700 ℃ as shown in (Figure 3a) and (Figure 3b) demonstrate the surface characterization of both metal oxides that is indicative to the activation sites associated with monolith surface morphology. For ZrO_2 mesoporous monolith we can see a terminal hydroxyl functional group 3550-3320 cm^{-1} this comes from the dissociation of water molecules during the sol-gel synthesis (Figure 3a). At wavenumber 2340 cm^{-1} this corresponds to capture of CO_2 due to the σ-coordination of the Lewis sites ability to abstract lone pair electrons attributed to the oxygen attached to CO bond in CO_2. The slightly massive valley peak at 698 cm^{-1} is associated with monoclinic crystal structure when annealed at 700℃. However there are not much variance with the HfO_2 mesoporous monoliths counterpart as shown in (Figure 3b) there is a clear capture of CO_2 peak at 2340 cm^{-1} and at 800-716 cm^{-1} wavenumbers attribute to HfO_2 monoclinic crystal structure when annealed at 700℃. The only distinction between ZrO_2 and HfO_2 mesoporous monoliths are moderate peaks at 1548 cm^{-1}- 1332 cm^{-1} which are bidentate bicarbonate and bidentate carbonate respectfully which come from ligand formation attributive to the coordinates of formic acid to Hf ions from the hydrolysis of NMF during sol-gel synthesis of the mesoporous monolith.

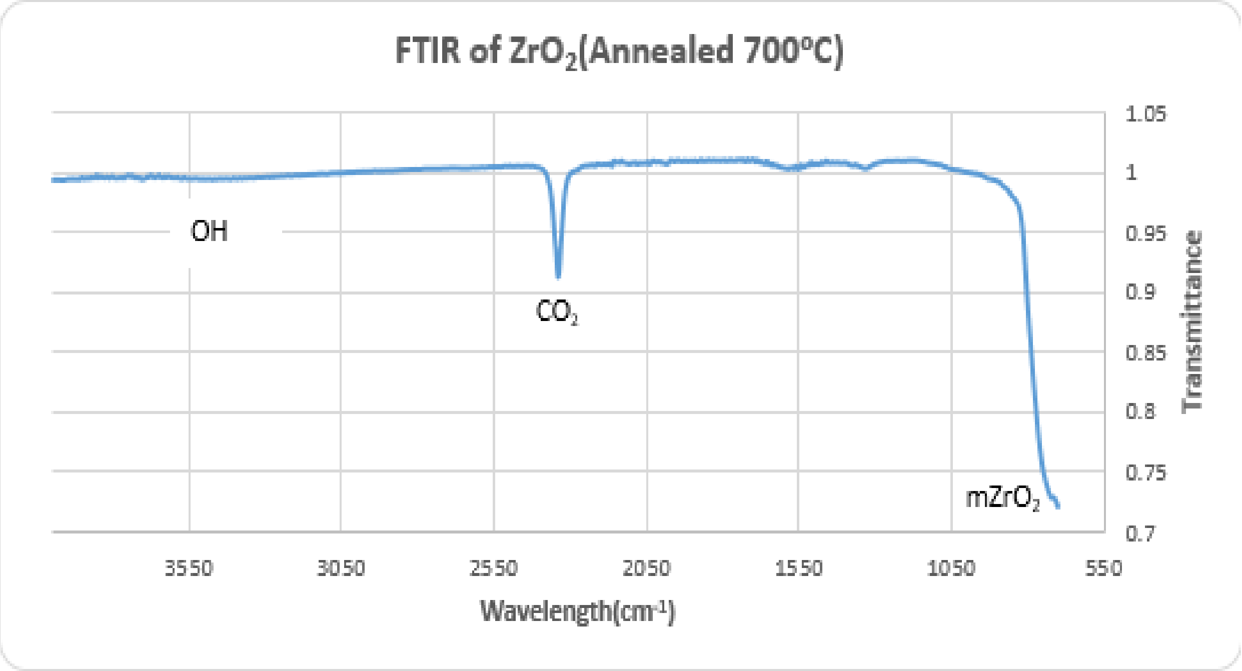

Figure 3a: *FTIR of monoclinic mesoporous* ZrO_2 *annealed at 700℃*

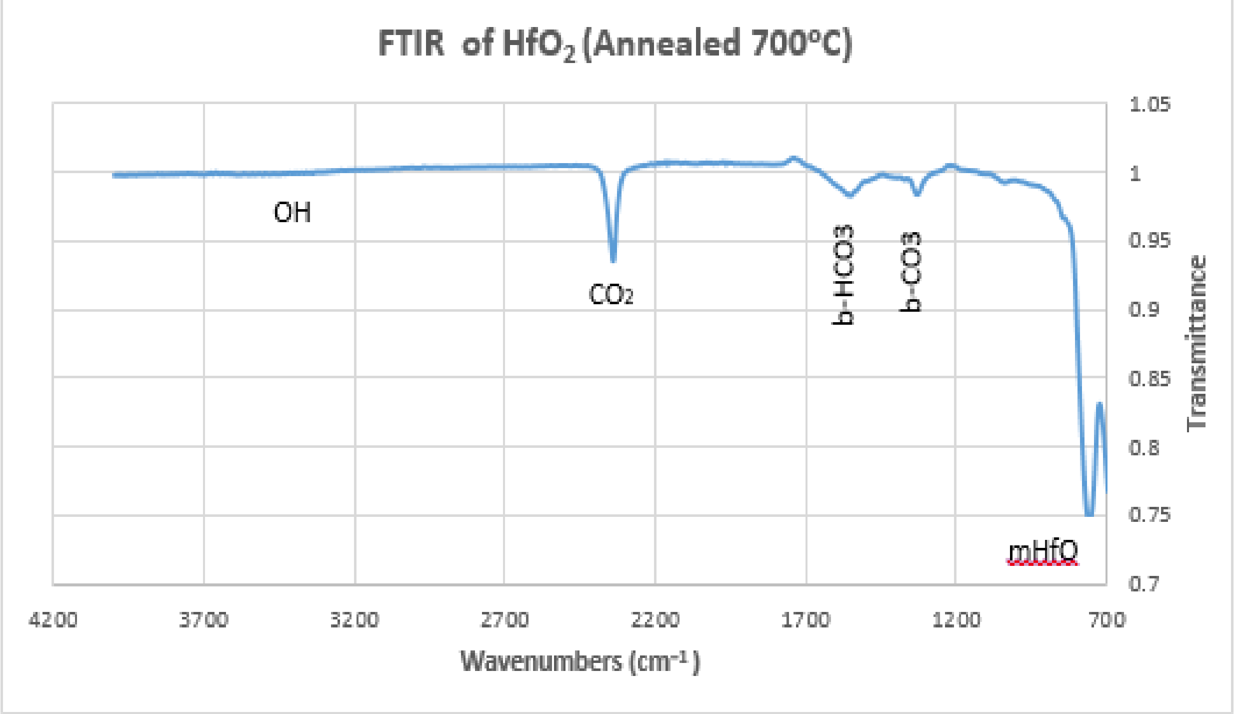

Figure 3b: *FTIR of monoclinic mesoporous* HfO_2 *annealed at 700℃*

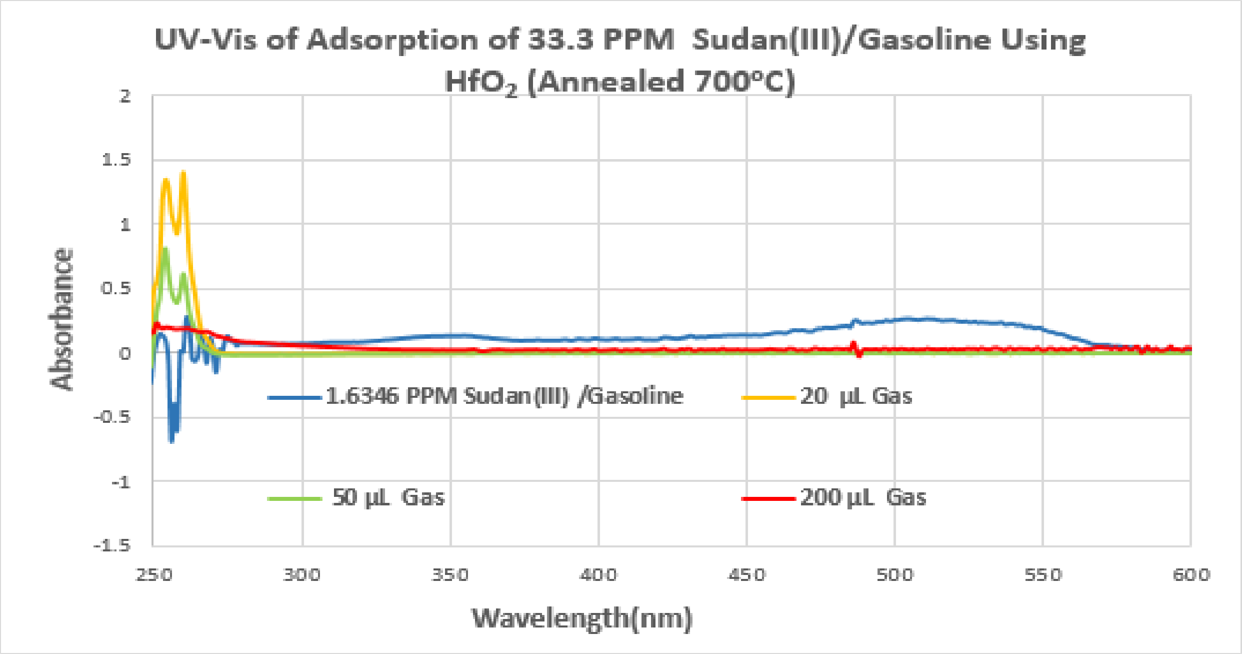

Figure 4a: *UV-VIS Adsorption of 33.3 PPM Sudan (III)/Gasoline Using* HfO_2 *(Annealed 700°C) at various volumes (20, 50, 200 µL) at surface of nano-pore water.*

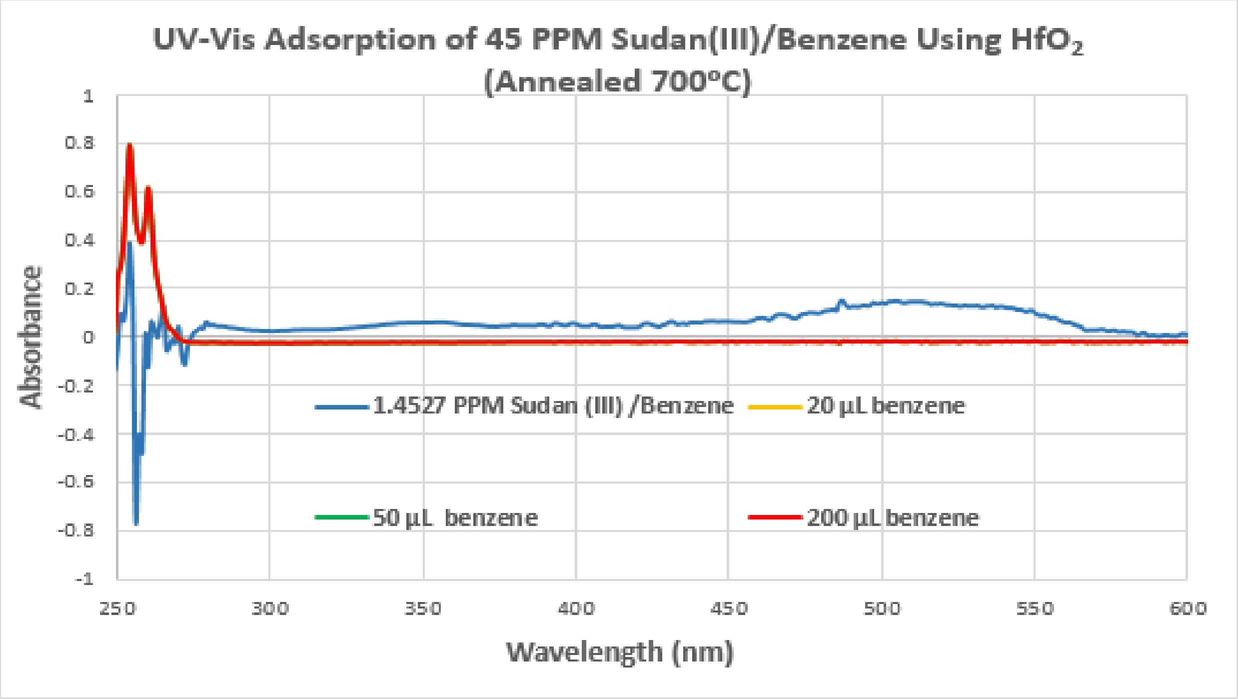

Figure 4b: *UV-VIS adsorption of 45 PPM Sudan (III)/Gasoline Using* HfO_2 *(Annealed 700°C) at various volumes (20, 50, 200 µL) at surface of nano-pore water.*

Ultraviolet visible (UV) spectroscopy was implemented to analyze the surface liquid after adsorption of 33.3 PPM Sudan (III)/Gasoline solution and 45 PPM Sudan (III)/Benzene using HfO_2 mesoporous monolith annealed at 700℃ as shown in (Figure 4. a-b). Similar UV spectroscopy results were seen for 30 PPM Sudan(III)/Methanol, 31.26 PPM Sudan(III)/Toluene solutions. Sudan (III) is shown to have a maximum absorbance at 508-512 nm even at very dilute concentration approximating 1 PPM of both Sudan (III)/Gasoline and Sudan (III)/Benzene as indicated by the blue curve, yet every other surface liquid samples that was subject to adsorption of various volume of dye/organics (20, 50, 200 μL) at the surface of water had a relative flat or no absorbance at 508-512 nm meaning there was a complete removal after exposing HfO_2 mesoporous monoliths for 1-2 minutes to the dye/organic surface layer. The flat indicates that the relative liquid samples did not contained any dye/organic solution rather each sample had the same spectra as the nano-pure water absorbance. Degradation was not seen during this experiment and monoliths used varied in size and surface area, therefore data collected were simply qualitative.

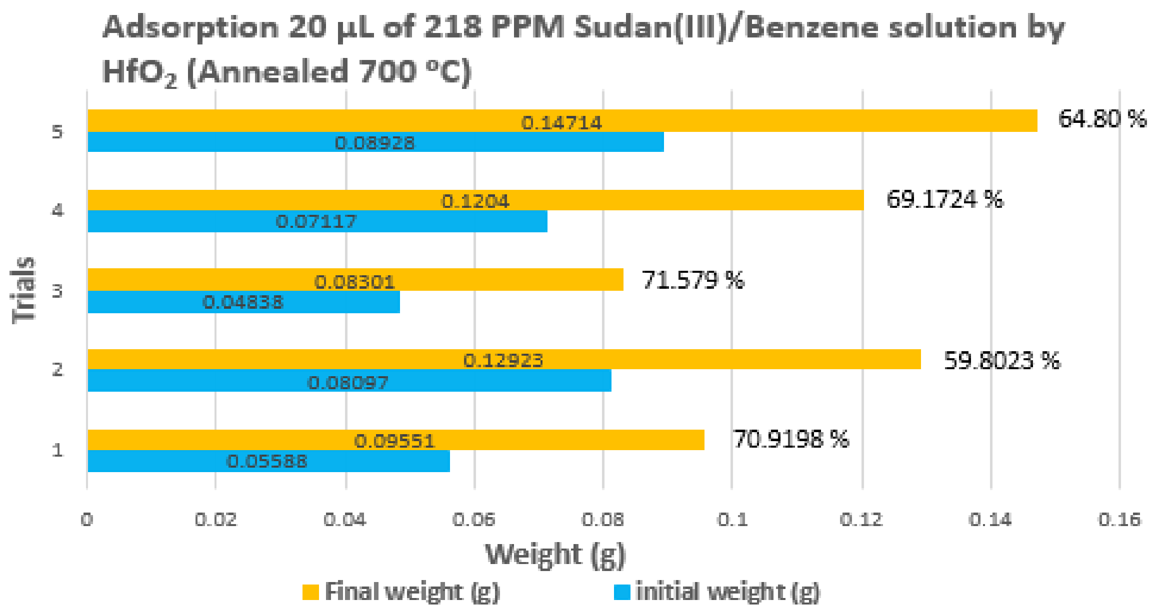

Figure 8a: *Preliminary Adsorption Capacity of HfO_2 (Annealed 700 ℃) removing 20 µL of 218 PPM Sudan (III)/Benzene solution from the surface of nano-water.*

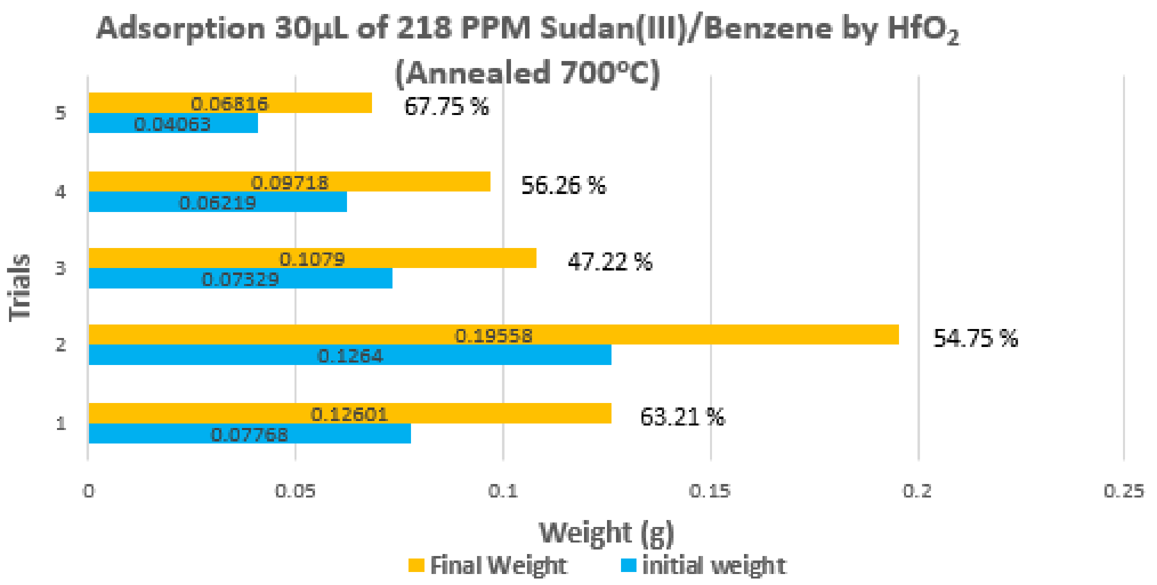

Figure 8b*: Preliminary Adsorption Capacity of* HfO_2 *(Annealed 700 ℃) removing 30 µL of 218 PPM Sudan (III)/Benzene solution from the surface of nano-pure water.*

Absorption kinetics studies of 218 PPM Sudan (III)/Benzene solution using five samples HfO_2 mesoporous monolith annealed at 700 ℃ having a range of average weight of 0.069-0.076 (g) after removal of the Sudan (III) / Benzene surface layer the average increase weight percent of the HfO_2 samples after adsorbing 20 μL was 67.22% data collected from the average percent adsorption capacity (Figure 8a). Similar results showed an average percent adsorption capacity of 57.63 % after absorbing 30 mL of Sudan (III) /Benzene surface layer (Figure 8a-b). It should be noted that the sample used in this experiment where not uniformed and contained fracture sites that effect the adsorption capability of the HfO_2 mesoporous monolith. Record time measurements from this study showed an average time for the set of HfO_2 samples capable to adsorb 20 µL at 53.2 seconds while the other set of sample was capable to adsorb 30 µL at 60.4 seconds. Although the ratio between 20 µL mass of benzene and mass of HfO_2 is approximately 1 to 1000 the results demonstrate the capacity for such monoliths to remove surface organic liquids from a hydrophilic solvent such as water.

Conclusion

It's indicative to say that HfO_2 and ZrO_2 mesoporous monoliths as a high potential adsorption capability of organics from the surface of water has a potential alternative material for water remediation. Data collected from UV-Vis of HfO_2 mesoporous monolith showed complete removal of a wide range of organic contaminants such as Benzene and Gasoline. (Figure 4. a-b). FTIR spectra of ZrO_2 and HfO_2 showed different type of surface functional groups, yet further studies are needed to analyze such functional characteristic to propose potential adsorption mechanism attribute to any hydrophobic ligands adsorb on the pore surface of such metal oxide monoliths. The study of adsorption kinetics of the HfO_2 monolith showed the affinity for organic's on the surface of such monoliths having a relatively high average percent adsorption capacity of approximately 57-67 % after less than a 1 minute exposure to the liquid organic/water surface. Due to the organic contaminates adsorb to the surface pores rigid monoclinic crystalline network of the metal oxide monoliths evaporation can be implemented to remove organic as potential method to reuse metal oxide monoliths making them less susceptible to mechanical degradation unlike hydrogels and aerogels polymers. Studies of HfO_2 and ZrO_2 monoliths periodic degradation under extreme conditions on the surface water must be explored further in order to consider such alternative material for water remediation. Our sol-gel synthesis method allows metal oxide monoliths to be scalable for industrial manufacturing, yet future studies are needed in order for such materials to be implement for large scale removal of such organic contaminants from the surface of water.

Reference

1. *"Gulf Oil Spill."* Oil and Chemical Spills/Significant Incidents/Deepwater Horizon Oil Spill.N.p,02 Mar.2013.Web.03 June 2017.http://response.restoration.noaa.gov//deepwater-horizon-oil-spill.
2. *Macroscopic Multifunctional Graphene-Based Hydrogel and Aerogels by the Metal Ion Induced Self-Assembly Process*. Huai-ping Cong,Xiao-Chen Ren,Ping Wang, and Shu-Hung Yu. Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry, National Synchrotron Radiation Laboratory, University of Science and Technology of Chin, Hefei AnHui 230026, People's Republic of China. Vo.6, No.3 2012.
3. *Scalable Seashell-Based Chemical Vapor Deposition Growth of Three-Dimensional Graphene Foams for Oil−Water Separation.* Liurong Shi, Ke Chen, Ran Du, Alicja Bachmatiuk, Mark Hermann Rümmeli, Kongwei Xie, Youyuan Huang, Yanfeng Zhang, and Zhongfan Liu, Center for Nanochemistry (CNC), Beijing Science and Engineering Center for Nanocarbons, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Sklodowskiej 34, Zabrze 41-819, Poland, IFW Dresden, 20 Helmholtz Strasse, Dresden 01069, Germany, School of Energy, Soochow University, Suzhou 215006, P. R. China, BTR New Energy Materials Inc., Shenzhen 518106, P. R. China Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China
4. *Preparation and Photocatalytic Activity of Robust Titania Monoliths for Water Remediation.* Kazuya Nakata, Tomoya Kagawa, Munetoshi Sakai, Shanhu Liu, Tsuyoshi Ochiai, Hideki Sakai, Taketoshi Murakami, Masahiko Abe, and Akira Fujishima,Photocatalyst group, Kanagawa Academy of Science and Technology, KSP Building East 412, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan. Research Institute for Science and Technology, Energy and Environment Photocatalyst Research Division, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda 278-8510, Japan
5. *Novel hydrophobic polyvinyl alcohol– formaldehyde foams for organic solvents absorption and effective separation*. Yanxiong Pan, b Weicai Wang,ab Chao Peng,a Kai Shi,a Yunxia Luoa and Xiangling Ji
6. *Metal Oxide Electrokinetic Micropumps & Capillary Electrophoresis of Biomolecules and Caron Based Nanomaterials*. Ivonne M. Ferrer Lassala. The University of Buffalo, New York, Department of Chemistry. Jun 3. 2013.
7. *Investigation of CO and CO_2 Adsorption on Tetragonal and Monoclinic Zirconia.* Pokrovski, K.; Jung, K. T.; Bell, A. T, Langmuir 2001, 17 (14), 4297-4303; (b) Jung, K. T.; Bell, A. T, An in Situ Infrared Study of Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over Zirconia. Journal of Catalysis 2001, 204 (2), 339-347; (c) Xie, S.; Bell, A. T., An in situ Raman study of dimethyl carbonate synthesis from carbon dioxide and methanol over zirconia. Catal.Lett. 2000, 70 (3,4),