TO: Texas Air Research Center (or Texas Hazardous Waste Research Center)

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SUBJECT: Final Report

PROJECT NUMBER: 513LUB0025H

PROJECT TITLE: Removal of Some Emerging Water Pollutants by L-3 Class Biosorbents

PROJECT PERIOD: 09/01/2013 – 07/15/2015

DATE: 02/03/2016

Up to 5 pages of progress report including the following sections:

Project Description: The presence of unconventional water contaminants in the environment is a growing concern for the human health and the ecosystem. With technological development, and increased industrial, agricultural and domestic activities, the use of these emerging water contaminants (EWC), such as personal care products, pharmaceuticals, and herbicides/pesticides are increasing in our daily life, and the soil and water are getting contaminated with chemicals emerging from these sources. They need to be removed efficiently, and in environment-friendly way. Low cost, Locally available, and Low technologically prepared and used (L-3 class) biosorbents were investigated in this project for removal of some selected EWC's.

Wastewater needs to be purified by easy, and environment-friendly way. Adsorption is the most effective way to do it. L-3 biosorbents, such as peels of citrus fruits are taken from locally available biowaste. They are of low cost. Above all, they require very low technology to be prepared, and used. These very user-friendly biofilters can be used anywhere, especially they can have very high demand in remote, arid, and underdeveloped places of the world.

Objectives: The objectives of this proposal were the following: 1.Investigate and optimize the removal efficiency of biosorbents prepared from biowaste (peel of citrus and non-citrus fruits) for phenols (cresol and 2,4-dinitrophenol), pharmaceuticals (tylenol, ibuprufin, and amoxicillin, and testosterone), and herbicides/pesticides (tebuthiron, and imidaclorpid) in water. We included later on diphenhydramine, aspirin (pharmaceuticals), and triclosan (antibacterial agent). 2. Study the effect of the following parameters in removal efficiency: equilibration time, pH, temperature, and ratio between adsorbate and adsorbent. 3. Study the kinetics and mechanism of the contaminant removal processes. 4. Make tea-bags filled with optimal amount of biosorbents so that they can be used in remote areas for water treatment.

Methodology: We are mainly used citrus types of biowaste for making the biosorbents. This includes peels of different types of fruits, such as oranges, grapefruits, lime, lemon, and banana (non-citrus fruit). These fruit peels are loaded with principally pectin, which is responsible for removal of water pollutants. We made the biosorbents by drying the peels in the sun for several days, and then crushed them into powders. We used these biosorbents to treat water containing phenols (cresol, and 2,4-dinitrophenol), and pharmaceuticals (tylenol, ibuprofen, amoxicillin, and testosterone). We used UV-vis spectroscopy, and LC/MS/MS instrument to find the optimum removal efficiency of the above water contaminants by changing equilibration time, pH, temperature, and the amount ratio between contaminants and biosorbents. We made tea bags filled with optimal biosorbents so that they can be used for water treatment simply by stirring the tea-bags in contaminated water.

Accomplishments/Problems:

During our investigation within the project period, we achieved the following accomplishments:

1. Preparation of Powders of Citrous Fruits: We collected biowaste of citrus fruits, such as orange, lime, and grapefruits, and dried and crushed. They were used for treatment work.

2. Materials Characterization of Biosorbents: Scanning Electron Microscopy and Energy Dispersive X-ray Analysis were performed on the biosorbents to understand their morphology, and identify the elements present in the biosorbents. Figure 1 shows the SEM images for pure orange peel powder (OPP) and OPP with amoxicillin, diphenhydramine and acetamenophen separately. OPP images clearly shows scale/layer like appearance that possibly provides more sorption sites and higher surface area. EDAX image of OPP shows the presence of potassium and calcium ions in addition to carbon and oxygen. Compared to grapefruit peel powder, OPP has flake/leaf like structures containing grains, whereas grapefruit peel powder contains rod-like

matters. Both of them contains potassium and calcium ions in addition to carbon and oxygen, but for orange peel the amount of K and Ca are about 10 times lower than those in grapefruit. Other images with EWC's indicate how the morphology of OPP modifies after the adsorption of EWC's.

X-ray diffraction patterns were also obtained for OPP and with six EWCs. We do not much differential diffraction peaks were observed, except for OPP with 2,4-dinitrophenolexpect that shows amorphous broad peak at 22.5° 2-theta value (Figure 2).

3. Study on Removal Efficiency of Selected Pharaceuticals: A simple, rapid and economical method was developed for removal of analgesic drugs, steroids and antibiotics from water using orange peel powder (OPP). The analysis was carried out using Agilent 6460C LC/MS/MS with a QQQ detector. The Standard solutions of amoxicillin, diphenhydramine, acetaminophen, aspirin (acetylsalicylic acid), and 19-nortestosterone in the concentration range of 0.5-10 ppm were prepared using water or water/acetonitrile as solvents. Calibration curves for these EWC's shows correlation coefficient values in between 0.90-0.99. Orange peel powder of different amount was added in the synthetic water containing 1-10 ppm of the above emerging water contaminants, and kept the biosorbents at different residence times. Figure 3 shows exemplary the trends of removing testosterone at different amount of biosorbents, and at different residence time. In general, the adsorbate/adsorbent ratio lies in between 0.16-0.75 mg/g for 19-nortestosterone, and 0.01-0.23 mg/g for amoxicillin. 80% removal efficiency for testosterone was found when 5 g of OPP was used for 15 minutes. Similarly, 56% removal efficiency for amoxicillin was found when 5 g of OPP was used for 30 minutes. We also found leaching propensity of OPP when the residence time was increased.

The data were further processed for finding relationship of Langmuir isotherm. When 1/qe vs. Ce was plotted, it shows a linear relationship. Here, qe = mass of adsorbate/mass of adsorbent, and Ce = concentration of amoxicillin remaining in the solution phase. The plots show correlation coefficients of around 0.99 indicating that the adsorption process possibly obeys Langmuir relationship. Calculations are in progress to performed on different adsorption isotherm models to delineate the adsorption mechanisms

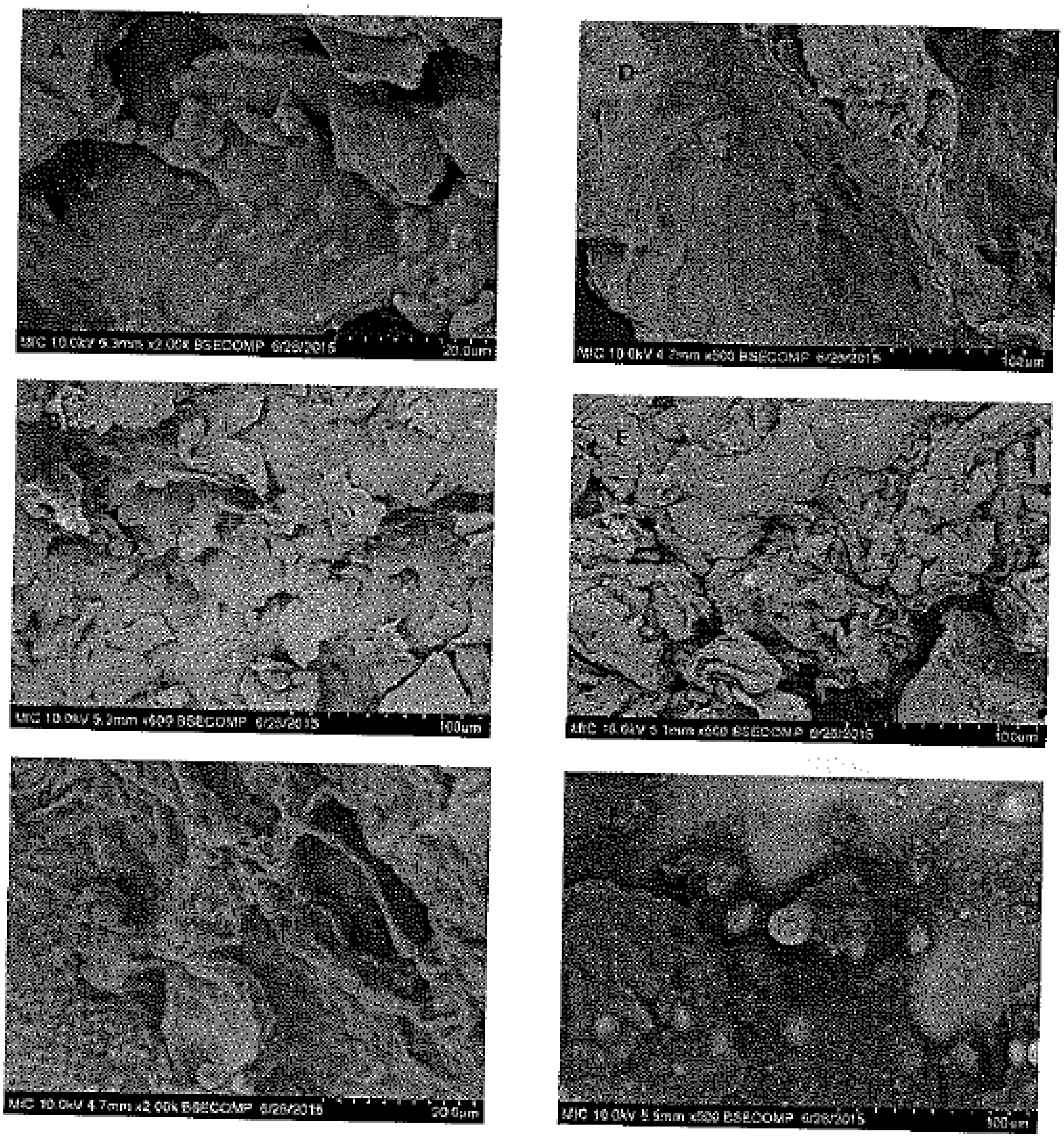

Fig. 1: SEM images of pure orange peel powder (OPP) and with other adsorbed EWC's at different magnification. From left top to bottom: OPP at 20 μm, OPP at 100 μm, and OPP with amoxicillin at 20 μm. Right top to bottom: OPP with amoxicillin at 100 μm, OPP with diphenylhydramine at 100 μm, and OPP with acetaminophen at 100 μm.

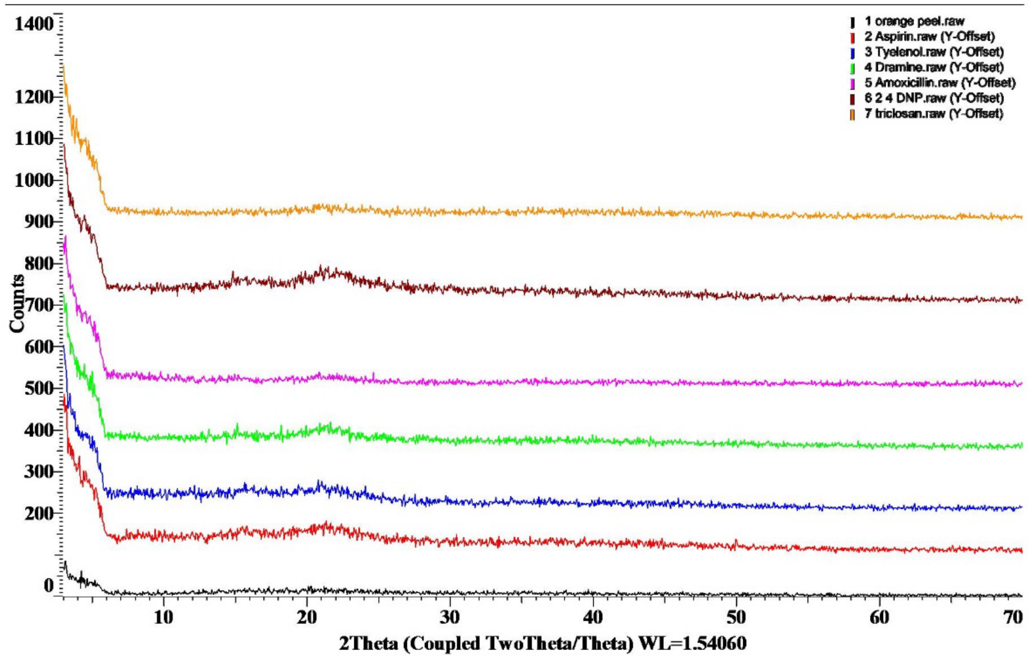

Figure 2. XRD for orange peel powder (OPP) and with other EWC's. From top to bottom: OPP with triclosan, OPP with 2,4-dinitrophenol, OPP with amoxicillin, OPP with diphenhydramine, OPP with acetaminophen, OPP with aspirin (acetylsalicylic acid), and pure OPP.

The data were further processed for finding relationship of Langmuir isotherm. When 1/qe vs. Ce was plotted, it shows a linear relationship. Here, qe = mass of adsorbate/mass of adsorbent, and Ce = concentration of 19-nortestosterone remaining in the solution phase. The plots show correlation coefficients of around 0.99 indicating that the adsorption process possibly obeys Langmuir relationship. .

For diphenhydramine, the Langmuir isotherm provides the following values: R^2: 0.89, and the binding constant as 5.0, whereas, the Freundlich isotherm provides R^2: 0.90, and the affinity constant as 2.2. Work is on progress on determining the maximum adsorption capacity per g of OPP for the investigated EWC's.

4. Problems: Due to presence of numerous organic chemicals in the biowaste, it was really challenging to use only LC to quantify the particular water contaminants. Fortunately, LC/MS/MS can filter all these artifacts away, and this instrument is wonderfully helped us to concentrate only on our intended chemicals. In addition, some of the chemicals we are described in the project description are not quite soluble in water. That is also another challenging aspect of this project.

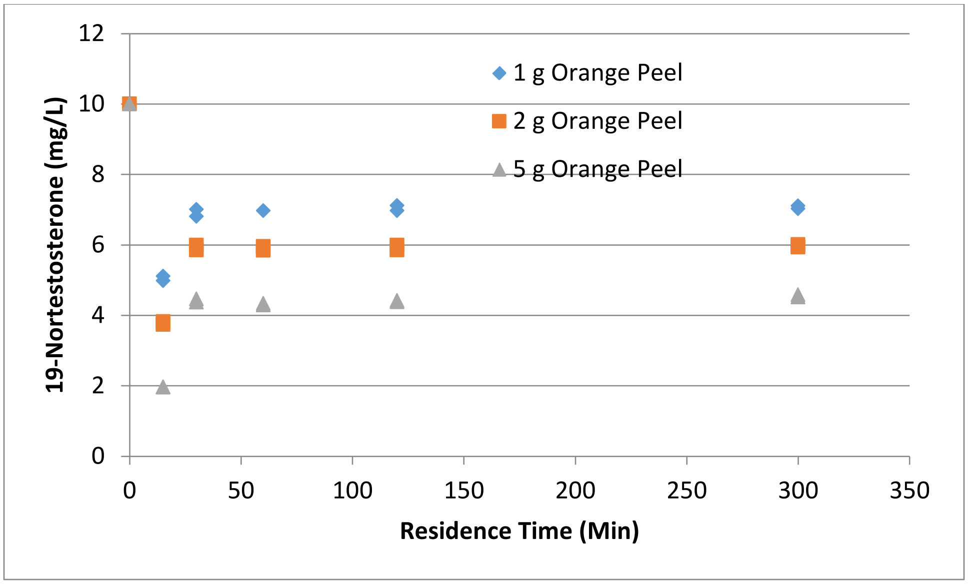

Figure 3. Removal of 19-Nortestosterone at different amount of adsorbents and residence time

5. Experiments with Cresol/2,4-Dinitrophenol: Our experiments with removal of cresol and 2,4-nitrophenol were not successful. These chemicals react with peel powder of citrus fruits, and produce precipitates, or solidify. Therefore, we could not use neither UV-Vis spectroscopy or LC/MS systems to study to removal efficiency. Probably, this high reactivity of these chemicals towards pectin makes them unsuitable as target species for biosorption.

Future Work:

1. We will identify the chemical structures of the precipitates that formed by cresol and 2,4-dinitrophenol and orange peel powder, and investigate the possibility of improving the absorptivity of OPP for these chemicals.
2. We will continue studying the removal efficiency of tebuthiron, and imidaclorpid by orange peel powder.
3. We will develop a low-cost filtering system using bisorbents.
4. We will spread the words about the benefits of using L-3 biosorbents for water treatments through World Wide Web, and networking.

List of Publications and Presentations:

1. Raghuveer Painam, A Study of the Removal of Pharmaceuticals and Other Emerging Pollutants in Drinking Water Using Orange Peel Powder, M.S. Dissertation, Department of Chemistry, Lamar University, December, 2015.

2. Andrew Gomes, Raghuveer Painam, Rakesh Revoori, Shyam Shukla, Removal of steroids and antibiotics from water using orange peel powder, Paper #223, 2014 Southwest Regional Meeting (SWRM), American Chemical Society, Fort Worth, TX, November 19-22, 2014.
3. Carra Curtice, Andrew Gomes, Shyam Shukla, Determination of Pesticides in Conventional and Organic Tomatoes, Lamar University Undergraduate Research Expo, poster presentation, Beaumont, TX, April 20, 2015 (Received 1st prize in Science Division in 2015 Lamar University Undergraduate Research Expo).
4. Andrew Gomes, Shyam Shukla, Sequester of Water Contaminants by Biowaste, Invited Speaker, Golden Triangle Sierra Club, Beaumont, TX, February 03, 2015.
5. Raghuveer Painam, Shyam Shukla, Alka Shukla, Andrew Gomes, L-3 Class Biosorbents and Removal of Pharmaceuticals from Contaminated Water, graphic-form presentation, Department of Chemistry & Biochemistry, Lamar University, Beaumont, TX, November 4, 2014.
6. Planning to present two presentations orally at 20th Annual Green Chemistry and Engineering Conference, Portland, Oregon, June 14-16, 2016.
7. Andrew Gomes, Shyam Shukla, Raghuveer Painam, Removal of Some Selected Emerging Water Contaminants Using L-3 Biosorbents, Work in Progress, for submitting to Journal of Hazardous Materials.