

TO: Texas Hazardous Waste Research Center

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SUBJECT: Annual Progress 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: 09/15/2014

Project Description: With technological development, and increased industrial, agricultural and domestic activities, such as the use of personal care products, pharmaceuticals, and herbicides/pesticides in our daily life, 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 can be one of the best choices.

Wastewater needs to be purified by easy, and environment-friendly way. Adsorption is the most effective way to do it. L-3 biosorbents 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 are 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, ibuprofen, and amoxicillin, and

testosterone), and herbicides/pesticides (tebuthion, and imidacloprid) in water. 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 using 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 will use these biosorbents to treat water containing phenols (cresol, and 2,4-dinitrophenol), pharmaceuticals (tylenol, ibuprofen, amoxicillin, and testosterone), and herbicides/pesticides (tebuthion, and imidacloprid). We are using 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 pollutants and biosorbents. We also plan to make 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:

Due to unavailability of proper instrumentations, our progress of work was delayed. As soon Lamar University has physically acquired an LC/MS/MS instrument, the progress rate in our work goes upward. In the last 12 months, we have achieved the following accomplishments:

1. Preparation of Powders of Citrous Fruits: We have collected biowaste of citrus fruits, such as orange, lime, and grapefruits, and dried and crushed. They are now ready 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/EDS for grapefruit peel powder, and Figure 2 shows the SEM/EDS for orange peel powder. Both of them shows flake/leaf like structures containing either grains (for orange peel), or rod-like (for grapefruit peel) 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.

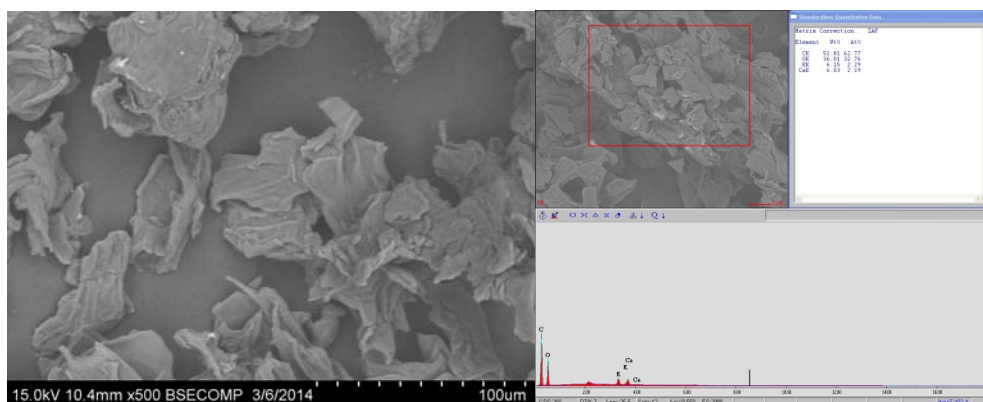


Figure 1. SEM/EDS for Grape Fruit Peel Powder

X-ray diffraction patterns were also obtained for both of these biosorbents. But no differentiable peaks were observed, expect broad peak for amorphous nature. (Figure 3).

3. Study on Removal Efficiency of Amoxicillin and 19-Nortestosterone: A simple, rapid and economical method is planning to develop for removal of 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 19-nortestosterone and amoxicillin in the concentration range of 2-10 ppm were prepared using water as solvent. Figure 4 and 5 show the calibration curves for these two water contaminants with correlation coefficient values in between 0.98-0.99. 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 6 shows 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. Preliminarily, we also found leaching propensity of OPP when the residence time was increased.

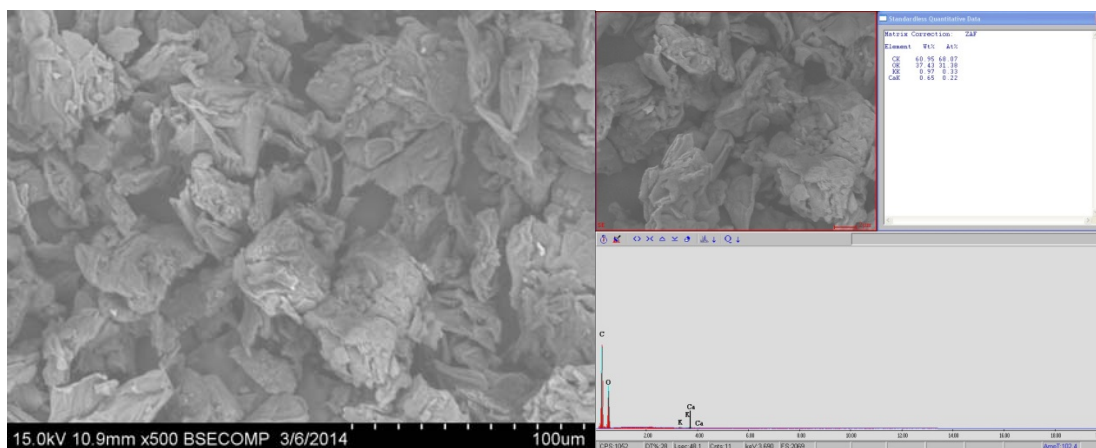


Figure 2. SEM/EDS for Orange Peel Powder

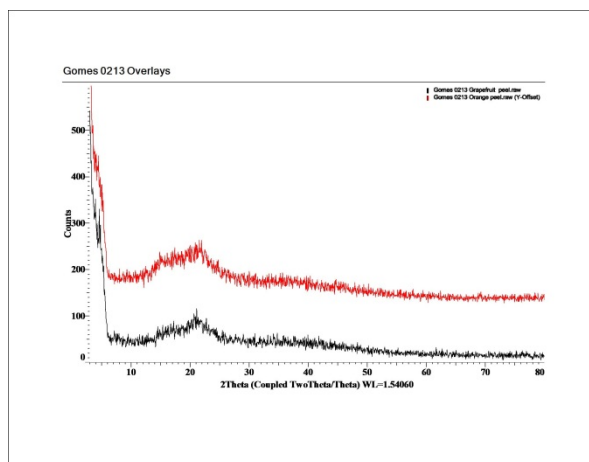


Figure 3. XRD for orange peel powder and grapefruit powder.

The data were further processed for finding relationship of Langmuir isotherm. When $1/q_e$ vs. C_e was plotted, it shows a linear relationship. Here, q_e = mass of adsorbate/mass of adsorbent, and C_e = 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. 1. Calculations are in progress to performed on different adsorption isotherm models to delineate the adsorption mechanisms.

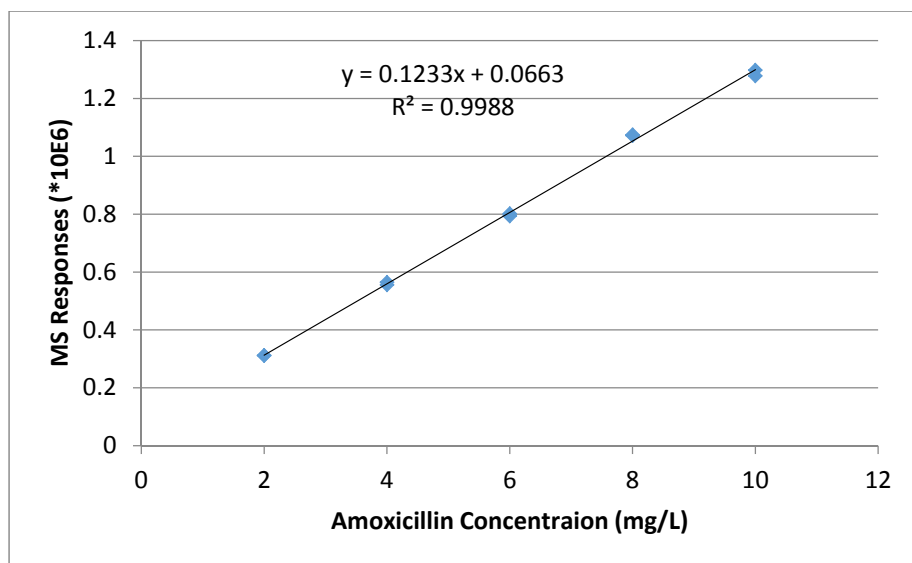


Figure 4. Calibration curve for Amoxicillin

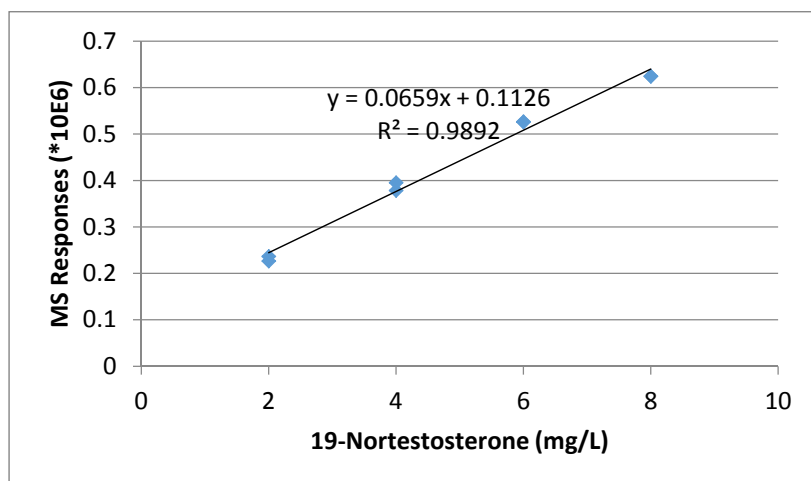


Figure 5. Calibration curve for 19-Nortestosterone

The data were further processed for finding relationship of Langmuir isotherm. When $1/q_e$ vs. C_e was plotted, it shows a linear relationship. Here, q_e = mass of adsorbate/mass of adsorbent, and C_e = 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. We are continuing work on this calculation to look for other isotherm relationships.

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.

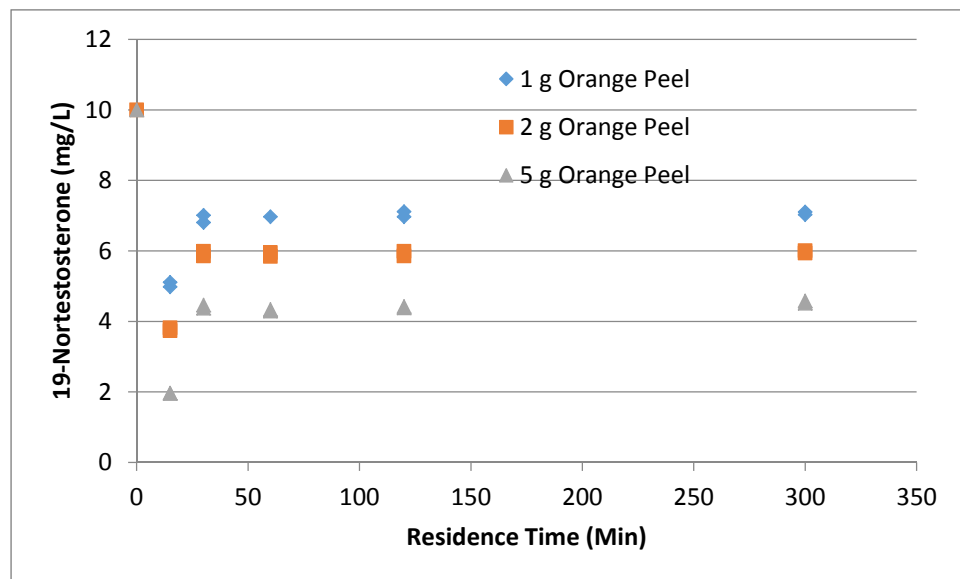


Figure 6. Removal of testosterone at different amount of adsorbents and residence time

Future Work:

1. We will work on cresol and 2,4-dinitrophenol, Tylenol and Ibuprofen, tebuthiron, and imidacloprid,
2. Investigate of Reaction Mechanisms, and
3. Performance Test with Tea Bags

List of Publications and Presentations:

1. Andrew Gomes, Raghuveer Painam, Rakesh Revoori, Shyam Shukla, Removal of Steroids and Antibiotics from water using Orange Peel Powder, Abstract submitted to Southwest Regional Meeting of ACS, Fort Worth/Dallas, TX, November 19-22, 2014.
2. Planning to submit a graphic form presentation at 19th Annual Green Chemistry and Engineering Conference, North Bethesda, MD, June 14-16, 2015.