Project Proposal

1. **Title of Proposal:** Reusable Magnetic Janus Particle Scavengers for Environmentally-Friendly Remediation of Contaminated Water Bodies.
2. **Focus Category:** Non point pollution, toxic substances, water quality
3. **Keywords** Janus Particle, Emulsion, Oil Remediation, Heavy Metal, Magnetism, Surface Water
4. **Duration:** March 1, 2011 through February 28, 2012
5. **Federal Funds Requested.** $5,000
6. **Non-Federal (matching) Funds Pledged.** $10,055
7. **Principal Investigator (graduate student).**
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9. **Congressional District(s) where project will occur:** 17
10. **Abstract.**

Industrial waste containing chemicals and heavy metals, as well as concern over the fate of oil released from the recent BP Deepwater Horizon rig accident are problems facing the Texan water supply that need to be addressed. A novel magnetite Janus particle scavenger is proposed as emulsifier to be used in place of current surfactants for remediation of contaminated water bodies. These reusable particles have environmental and economic advantages over the surfactants. The Janus particle, a compartmentalized colloidal particle with two chemically or physically different sides, can form stable emulsions that can entrap oil or heavy metals depending on the ligands attached to the particle. The emulsion can consequently be destabilized by application of a magnetic field which will allow recovery and recycling of the particles and collection and disposal of the toxic waste including oil or heavy metals. Various functionalizations of magnetite Janus particles will be tested in the lab for emulsion stability and efficacy of oil, chemicals and heavy metals release, and will be finally used in the field in contaminated estuary, wetland and waterway samples.

11. **Statement of Critical Regional Water Problems.**

Chemical & Nuclear Plants, Oil refineries, pipe-lines and off-shore drilling pose an increased risk to the water supply of the state of Texas. The recent explosion of BP Deepwater Horizon rig released 4,928,100 barrels of oil from the Macondo well into the Gulf of Mexico with an error margin of 10% (1). While a large portion of this oil has been recovered or eliminated, 1,281,306 barrels, or 26% of the total amount (1), is unaccounted for and could potentially wash ashore, contaminating estuaries and wetlands. Water pollution in major Texan estuaries is an ongoing problem. An example can be cited of Sabine-Neches Estuary in Beaumont, Texas. It receives wastewater effluents from 160 industrial and municipal treatment plants. Trace elements detected in the water include lead, zinc, cobalt, nickel, copper and chromium (2). Apart from the afore mentioned trace metal contaminants Brazos River Authority in its website states that arsenic contamination in Fin Feather Lake and Bryan Municipal Lake exceeds the human health criterion for water and fish (3). A 2007 study in quality of water in San Francisco Bay area found hormone disrupting chemicals like phthalates, bisphenol A and triclosan. The affects of these chemicals includes male infertility, female infertility and disruption of thyroid system (4). As similar chemical industries are present in Texas, for example in Baytown, the water bodies are likely to be

contaminated with these toxic substances also. As such removal of these chemicals by an environmental friendly way is of utmost importance.

Introduction of biologically-derived surfactants in recent years helped address some of the concerns regarding environmental toxicity. However, the inability to recover and recycle surfactant at the end of an operation is still a problem. We propose using Janus particles, or functionalized colloidal particles, to address this issue due to their increased emulsifier potential and possibility of reuse and recycling.

12. Nature, Scope, and Objectives of the Research.

Janus particles are compartmentalized colloidal particles with two sides of different chemistry or polarity (5). It is well-known that small particles can stabilize immiscible liquids forming so-called Pickering emulsions. Unlike surfactants, colloidal particles create more stable emulsions since more energy is required to remove them from the interface (6). Better yet, Janus particles offer a 3-fold emulsifier potential for water-oil emulsions over homogeneous colloidal particles in theoretical studies (7). A brief procedure of synthesis of Janus particles is mentioned as follows and shown in the schematic in figure 1:

1. Magnetite coated silica particles or iron oxide particles chosen for their low toxicity (8) are synthesized in lab and then are suspended in liquid wax at 75^0C. Water is added and an emulsion is formed as shown in figure 1.
2. The emulsion is cooled and then filtered.
3. Suitable solvent system is used to functionalize the exposed faces of the silica spheres to desired ligands.
4. Wax is then dissolved in chloroform and the functionalized silica particles retrieved.
5. The newly exposed surface of the silica can be further functionalized.

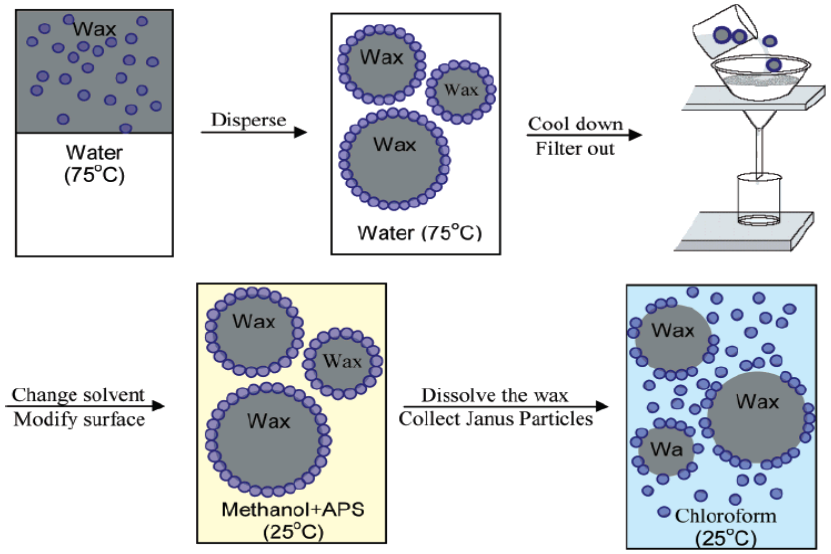

Figure 1: A schematic of the synthetic route to be followed in the lab to generate Janus Particle Scavengers (9)

Different ligands can be attached to the particle surface, and the functional group, length of ligand backbone and pH will influence the ultimate polarity and charge of the particle surface. The attached ligands can also have chelating properties, which can be used to complex and recover toxic heavy metals, oil and organic contaminants.

Janus particles can be functionalized to act as scavengers for trace elements in water. Thiol groups are known to be effective chelating agents for Pb, Cu, As, etc. We propose to functionalize Janus particles with ligands containing thiol group such as (3-mercapto) propyl trimethoxy silane so that they can bind heavy metals like Pb, Cu, As and Hg (10, 11). Also EDDS (ethylenediamine-N,N'-disuccinic acid) which is an environmentally friendly alternative to EDTA (12) can also be

functionalized on the silica particles. EDDS is an effective binder for heavy metals like Pd, Cu, Cr (III), etc. Toxic organic waste in water like phthalates can be recovered back by functionalizing Janus particle with polyaniline moieties. For oil remediation, functionalizing one face of the magnetized Janus particle with a hydrophobic group like n-octadecanetrichlorosilane will give surfactant-like property to the particles so they can solubilize the oil. On application of a strong magnetic field, these Janus particles will align, disrupting the emulsion to allow collection and disposal of the oil. This unique aspect is not present in surfactants. While surfactants disperse oil in water, they cannot be recovered or reused. Magnetized Janus particles, on the other hand, can not only stabilize contaminants in water emulsions but can also retrieve them by breaking the emulsion to ultimately be reused in further water remediation. The following schematic in figure 2 shows the formation and breaking of emulsions by Janus particles and the mechanism being proposed for purification of estuary water bodies from various contaminants.

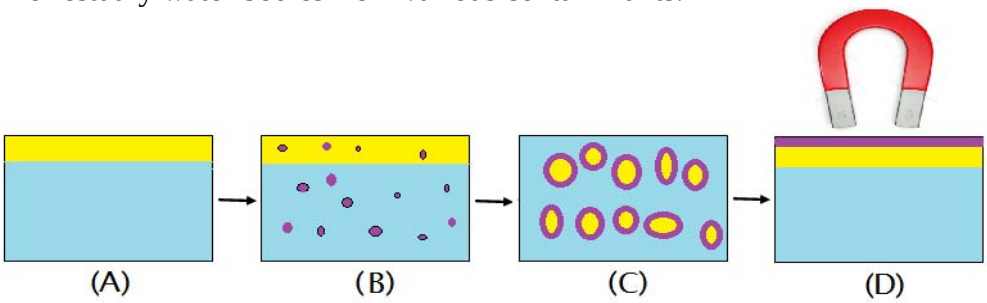

Figure 2: Picture (A) shows two immiscible liquids not yet emulsified. Picture (B) shows magnetized Janus particles being added to the system. Picture (C) shows stabilized Pickering emulsion being formed by the Janus particles dispersing the yellow liquid in the blue one. Picture (D) shows the magnetic Janus particles being aligned by application of magnetic field destabilizing the emulsion system and easy recovery of the yellow liquid and reuse of the particles.

First, we will test the emulsifier efficacy of the magnetite Janus particles in various oil suspensions by varying their diameter and the type of ligands attached. Visual observation, rheological changes, sensitivity to turbulence and zeta potential of the emulsion over time, temperature, concentration and pH range will help quantify this. The type of emulsion, oil-in-water or water-in-oil, will also be tested via the dye solubility test. Then, the strength and duration of magnetic field needed to destabilize the emulsion to release the oil or heavy metal will then be optimized for the chosen magnetite Janus particles with a magnetometer. Next, samples from oil-polluted wetlands and estuaries will be collected and tested for remediation using magnetite Janus particles. The ultimate goal would be to use these magnetic Janus particles on a large scale for economic and environmentally-friendly oil and toxic chemical remediation. In this case, construction of refining facility beside an estuary with a large reservoir will allow continuous water uptake, filtration, Janus particle injection and emulsion formation, followed by application of magnetic field with oil recovery and Janus particle recycling via fine filtration and subsequent release of clean water back to the estuary.

13. Results Expected from this Project.

A novel way to treat Texan water supplies for oil and heavy metal contamination with magnetite Janus particles is expected which will have superior emulsification capabilities over currently used surfactants and chelating agents. More importantly, these particles can be repeatedly reused which makes them environmentally and economically friendly because there is no need to employ new particles for every remediation. Once a fundamental study of the magnetite Janus particles is complete, the optimal particle system will be tested for heavy metals, oil, and toxic organic waste remediation from industrial release and non-point pollution water samples.

References

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