1. **Title of the Project:** Synthesis of Polymer Nano Hydrogel and Development hybrid wastewater treatment system using Cavitation Technique and Hydrogel.
2. **Number and date of Sanction letter:** F. No. 10-1/2010-CT (WM), dated 28/12/2013
3. **Duration of the Project:** 2 years 7 months (Including extended period)
4. **Total outlay of the Project:** Rs.34,29,300/-
5. **Date of start of Project:** 28-12-2013
6. **Date of completion of Project:** 31-07-2016

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1. Brief introduction

Hydrogels are three dimensionally dense cross linked polymer network structures composed of functional hydrophilic groups which have the ability to absorb significant amount of water and solute molecules. Hydrogels are also known as smart materials which show response and swelling when there is small change in external environment. The response of hydrogel is dependent on the presence of hydrophilic functional groups such as –OH, –COOH. These groups make the hydrogel hydrophilic and due to capillary action and difference in the osmotic pressure, water diffuses into the hydrogel. A number of adsorbents are used in dye adsorption, e.g. activated charcoal, clay materials such as bentonite, flyash, kaolin and montmorillonite. These adsorbents generate secondary waste and some of the materials are not efficient adsorbents because of their limitations in the cation exchange capacity, lower adsorption rate, etc. Hence, the enhancement of adsorption process has been achieved using cavitation, changing cation exchange capacity or hybrid nanocomposites. Nanocomposite hydrogels are loaded with the different types of clays like bentonite, Kaolin have been studied in this project for removal of various dyes such as crystal violet, Malachite green and brilliant green. In this project, Ultrasonic irradiation is used to initiate the emulsion polymerization to form hydrogel through the generation of free radicals as well as the uniform distribution of clay across the hydrogel polymer matrix. Enhancement of adsorption process by combining it with ultrasonic cavitation has been studied at lab level. Hydrodynamic cavitation combined with packed bed hydrogel process has been developed with the aim of treatment of bulk quantity of wastewater.

2. Objectives

- Synthesis of polymer hydrogel and incorporation of nanoparticles into the polymer matrix.
- Comparative study of cavitation effect and gel adsorption onto model pollutants.
- Development of simplified process for removal of these textile dye compounds. Testing effectiveness of developed system for industrial waste water treatment.

3. Methodology adopted

Synthesis of poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite via ultrasound assisted in situ emulsion polymerization was carried out. The response of the nanocomposite hydrogel was evaluated using a cationic dye, crystal violet (CV) under different temperature, pH, and cavitation environment. Removal of brilliant green dye from water using a poly (acrylic acid) hydrogel composite (PAA-K hydrogel) prepared by incorporation of kaoline clay has been investigated. The composite has been synthesized using ultrasound assisted polymerization process as well as the conventional process. The optimum conditions for the removal of dye are pH: 7, temperature: 35 ^{0}C, initial dye concentration is 30 mg/L and hydrogel loading 1 g. Combined novel hybrid technique (hydrodynamic cavitation + hydrogels packed bed adsorption) has been studied for dye degradation and subsequent adsorption of dye molecules. A lab scale hybrid system consists of 5 L of capacity have been fabricated in in-house for carrying out the experiments. Polyacrylic acid (PAA)/nanocomposite hydrogels which includes PAA-Bentonite clay nanocomposite and PAA-Graphene oxide nanocomposite hydrogels have been synthesized via ultrasound assisted emulsion polymerization technique. Synthesized hydrogels have been characterized by XRD and TEM analysis. Operational parameters such as effect of inlet pressure, effect of bentonite clay content in PAA hydrogel, effect of hydrogel quantity loading in packed bed, effect of pH on removal of dye pollutants have been investigated using hybrid technique. Initially the azo type of dyes such as malachite green and crystal violet dye removal have been studied using the lab scale hybrid system.

4. Results / findings

Poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite has shown the maximum CV dye removal above 75 % in the pH range of 9 to 11. A maximum of about 87 % removal was obtained at 35 ^{0} C. 2 g of hydrogel sample loading in the reactor shows about 95 % of dye removal. Adsorption by hydrogel alone, obtained 87 % removal of CV dye in 15 h andwith combination of ultrasound 97 % removal was achieved in only 5 h.

In the case of poly (acrylic acid)-Kaolin (PAA-K) hydrogelcomposite for adsorption of brilliant greendye, the maximum adsorption takes place at pH value of 7.The maximum extent of removal obtainedat 35 ^{0}C

was 56.24 % for the conventional method and 88.3 % to 100%, was reached when 2 g of ultrasonically synthesized hydrogel was used. At the same time when the conventionally synthesized hydrogel was used, 2 g hydrogel was able to remove only 63 % dye. In the case of HC+Hydrogel, 49 %decolourization of Cv dye and 18 % of mineralization rate was achieved with the HC only. Extent of decolourization and mineralization of CV of dye was achieved from 49 to 75 % and 18 to 67 % respectively when; the hydrogels were combined with HC. At pH 2.4 the combined system has been removed 93 % of decolourization of Crystal violet dye. It has been found that the removal of Malachite Green dye is 96 % in the combined HC and Hydrogel than the single hydrodynamic cavitation technique.

5. Research output

1. Bhaskar Bethi, Shirish H. Sonawane, Bharat A. Bhanvase, Sarang Gumfekar, Nanomaterials based Advanced Oxidation Processes for Waste Water treatment: A review, Chemical Engineering Processing: Process Intensification, 109 (2016) 178-189.
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3. S.R. Shirsath, A.P. Hage, M. Zhou, S.H. Sonawane,M. Ashok kumar.Ultrasound assisted preparation of nanoclay Bentonite nanoclay-FeCo nanocomposite hybrid hydrogel: A potential responsive sorbent for removal of organic pollutant from water, Desalination, 281, 2011, Pages 429–4373.
4. Sachin R. Shirsath, Anup P. Patil, Rohit Patil, Jitendra B. Naik, Parag R. Gogate. Shirish H. Sonawane. Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly (acrylic acid) hydrogel loaded with kaolin clay: A comparative study. Ultrasonics Sonochemistry 20 (2013) 914–923.
5. S.R. Shirsath, D.V. Pinjari , P.R. Gogate , S.H. Sonawane, A. B. Pandit. Ultrasound assisted synthesis of doped TiO_2 nano-particles: Characterization and comparison of effectiveness for photocatalytic oxidation of dyestuff effluent, Ultrasonics Sonochemistry, 20, 1, (2013), 277-286.