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Intermolecular mechanistic treatment of recalcitrant environmental pollutants: Azo, benzene, naphthalene and vinyl sulfone

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ABSTRACT

A new class of coagulant, from natural resource namely laterite soil has demonstrated efficiency in degrading a wide range of industrial organic pollutants into simple hydrocarbon structures or less toxic compounds. The composition study revealed the relative Si/Al/Fe: 0.57/0.33/0.10 ratios in laterite soil and surface morphology of laterite soil were investigated to analyze the fundamental degradation that drive the decolorization of Reactive Black 5 (RB 5). The interfacial and colloid aspects of laterite soil colloidosomes and dye particles were distinguished with the corresponding mechanism of coagulation–flocculation process. RB5 structure was destabilized by activation of laterite soil colloidosomes through charge neutralization and subsequent siloxane polymerization through enhancement of siloxanes monomers. This research also evaluated the rate laws and reaction mechanism for each of the main chemical network strands of RB 5. The result implied that all the chemical network strands followed the pseudo first order of reactions. Research approach has utilized Fourier Transform Infrared Spectroscopy, Gas Chromatography Mass Spectrometry and Ultraviolet–visible Spectrophotometry (FTIR, GCMS and UV–vis) to study the degradation intermediates structure, chemical derivatives and final products after coagulation–flocculation process.

1. Introduction

Statistical analysis revealed that from year of 2009, industrial water consumption has reached up to 800 billion m^3 and the industrial water demand is continuously increasing at a high rate and projected a usage of 1500 billion m^3 industrial water by year of 2030. Rapid industrialization and development have led to increment of 87.5% industrial water consumption within 21 years. High consumption of industrial wastewater has perceived a great concern and attention. Textile industries show a rapid growth in the global market, accounted for 10.83% increment in exportation and investment [1]. According to United States Environmental Protection Agency for Pollution Prevention in the Textile Industry 1996, textile industry can take up to 200 L of water to produce 1 kg of textiles.

Synthetic dyes are widely used in textiles, cosmetics, leather, paper, and other similar industries which involve products coloration. Azo derivatives are the major class of dyes used in industries characterized with –N=N– structure, which is responsible for the color richness had posed a major pollution problem to environment due to color visibility and toxicity [2]. Azo dye molecules could not be broken down under the sunlight or radiant energy due to their high photolytic stable characteristic, thus critically affecting the aquatic system [3]. During degradation, azo dyes cleavages potentially generate aromatic amines. Some aromatic amines are considered carcinogenic since it can accumulate in the food chain and imperil human health and ecosystem [4].

Nowadays, the molecular structures of dyes have been altered in order to enhance the dye properties by improving delivery of dyes to fabrics, resistance to fade, and control the dye intensities. These properties make dyes resistance to complete degradation and potentially create degradation intermediates or by-products which is characterized as carcinogenic and mutagenic. Direct release of incompletely treated or degraded industrial dyeing effluent into the environment potentially arise massive impact to ecosystem as well contributing to environmental pollution and human health impact [5]. Therefore, different types of treatment methods such as adsorption [6], photocatalysis [7], photocatalytic under visible light irradiation [8], ozonation [9], plasma oxidation

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[10], membrane photoreactor [11], Fenton [12], sonophotocatalytic [13] to decolorize and degrade dyeing wastewater have been proposed and developed as alternative means.

Degradation pathways of dyes in coagulation–flocculation processes are yet to be explored. Researchers have focused their studies on coagulation since it is a physicochemical treatment process that shows high performance in treating dyeing wastewater. Various inorganic coagulants such as aluminum, ferric, magnesium salts and lime had been applied alone to treat dye wastewater. However, the sludge produced from inorganic coagulant is toxic. Flaten reported that aluminum is a neurotoxicant product that contributes to Alzheimer's disease [14]. Therefore, natural coagulants have recently received high degree of interest in treating dye wastewater.

In this study, a newly developed bi-functionalized coagulant–flocculant from natural resources—laterite soil was used to treat synthetic dyeing wastewater. Attempts were made to delineate the structural properties of laterite soil that initiate the decolorization of dyeing wastewater. The coagulation–flocculation experiments by applying laterite soil were conducted using a model Reactive Black 5 (RB 5) dye and a series of analysis was performed to understand the structural attributions leading to the degradation mechanism. In particular, the fragmentation of RB 5, nature of intermediates and reaction pathway were identified by UV–vis, FTIR and GCMS. The elucidation of silica (Si) based laterite soil in determining the rate laws of the main chemical network strands of RB 5 was also evaluated.

2. Methodology

2.1. Dye

The azo dye, Reactive Black 5 (RB 5) dye powder with molecular structure $C_{26}H_{21}N_5Na_4O_{19}S_6$ was supplied by Sigma–Aldrich. An aqueous stock solution of RB 5 was prepared by dissolving 1 g of RB 5 with deionized water using a 1 L volumetric flask. An appropriate amount of RB 5 from the stock solution was diluted to 500 mL with deionized water for coagulation–flocculation process.

2.2. Characterization of laterite soil

The surface morphology of laterite soil collected from Bukit Merah, Perlis, Malaysia was studied by using Scanning Electron Microscope (SEM) modeled JEOL JSM-6460 LA with a Schottky emitter at an accelerating voltage of 20 kV, probe current of 1.0 nA and energy range of 0–20 keV. The SEM is equipped with a Minicup EDS for X-ray Energy Dispersive Spectroscope (EDS) microanalysis to measure the chemical composition of laterite soil using ZAF method standardless quantitative analysis (oxide). The initial pH of laterite soil was tested by dissolving 20 g of laterite soil with 50 mL of deionized water in beaker, subsequently the calibrated pH meter was immersed into the beaker to measure the initial pH of laterite soil. The measurement showed the raw laterite soil carried a pH of 5.7.

2.3. Preparation of laterite soil

Initially, the reddish laterite soil was mixed with ultrapure water, then the mixtures were filtered with nylon cloth to remove any residues and impurities contained in laterite soil. Subsequently, the solution collected was dried in oven at 105 °C for about 2 h. The above procedures were repeated until the laterite soil was decolorized. Subsequently, the dried laterite soil was crushed into powder and sieved through 75 µm siever. The sieved laterite soil powder was mixed in ultrapure, followed by filtration to remove excessive fluid. Eventually, laterite soil paste collected on the filter paper was readily used as coagulant.

2.4. Batch coagulation–flocculation experiments for dye removal

Experiments on dye wastewater coagulation–flocculation process were performed using Jar-test equipment (JLT6 VELP Scientifica). From the previous study on laterite soil optimum pH, it was identified at pH 2 which was the point of zero charge (PZC) for laterite soil to be activated [15]. The initial pH of the solution was measured by 827 pH lab (Metrohm) and then adjusted to pH 2 using dilute HCl solution (0.01–0.1 M). The behavior of laterite soil in treating RB 5 was investigated by varying the dosages of laterite soil coagulant from 1000 to 14,000 mg/L. The mixtures were stirred rapidly at 200 rpm for 2 min, then decreased to 100 rpm for 15 min. Subsequently, the mixtures were allowed to settle for 30 min. 20 mL of samples were collected from the top of the settling beaker (2 cm beneath the water surface). The collected samples were filtered through Whatman filter papers and the filtrates were ready for analysis.

2.5. Analysis

The analyses were carried out in accordance with the Standard Methods for the Examination of Water and Wastewater. The UV–vis spectra of dye as a function of laterite soil dosages were recorded from 200 to 800 nm using Hitachi U-2810 Ultraviolet–visible Spectrophotometry (UV–vis). Absorbance peaks within the range of 400–800 nm represent visible region whereas absorbance peaks within the range of 200–400 nm represent ultraviolet region.

The Fourier Transform Infrared Spectroscopy (FTIR) measurement on the sludge was carried out at room temperature on a Nicolet iS10 Smart OMNI-transmission FTIR Spectrometer. The sludge produced after coagulation with laterite soil was collected and dried in the oven at 105 °C for 2 h. Solidified sludge was dried and ground into powder and dispersed in a matrix to mix with potassium bromide (KBr) solution. The mixture was transferred to a dye with a barrel diameter of 13 mm. Subsequently the dye was pressed to a disk form. The disk was removed carefully from the die and placed in the FTIR sample holder. The content in the disk was ready for the 4000–450 cm^{-1} transmission spectrum analysis. For the mechanism elutriation, the intermediate compounds for RB 5 was identified and analyzed with Shimadzu Gas Chromatography Mass Spectrometry (GCMS) GC 2010 Plus equipped with BPX 5 capillary column (30 m length, 0.25 mm thickness and 0.25 mm internal diameter). The supernatant after the coagulation–flocculation was extracted using dichloromethane. Helium was used as the carrier gas at 220 °C injection temperature. The column temperature was increased from 40 °C to 250 °C with 20 min holding time. Zeta potential of a solution was measured by using Zeta Meter 3.0 + Dispersion Technology.

3. Results and discussion

3.1. Characterization of laterite soil

Components consisting of laterite soil was identified by using Energy Dispersive X-ray (EDX) spectroscopy. The EDX spectra of laterite soil is shown graphically in Fig. 1. It is clearly indicating that laterite soil possessed substantial content of silica (Si), aluminum (Al) and iron (Fe). EDX reveals the relative Si/Al/Fe: 0.57/0.33/0.10 ratios in laterite soil whereby silica covered the highest percentage, followed by aluminum and iron. The morphology surface area of the laterite soil is shown in Fig. 2. The images represent the aggregation morphology of laterite soil. It can clearly observe that silica, aluminum and iron are randomly distributed on the solid surface

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