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Treatment of Terasil Red R and Cibacron Red R wastewater using extracted aluminum from red earth: Factorial design

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ABSTRACT

The ability of aluminum coagulant extracted from red earth to treat Terasil Red R (disperse) and Cibacron Red R (reactive) synthetic dye wastewater was studied. The effects of extractant concentration, soil-to-volume of extractant ratio, and the types of extracting agents (NaOH vs. KCl) on the concentration of aluminum extracted were also investigated. In addition, the efficiency of extracted aluminum was compared with aluminum sulfate, in terms of its capability to reduce the chemical oxygen demand (COD) and to remove synthetic color. Factorial design was applied to determine the effect of selected factors on the amount of aluminum extracted from red earth (i.e., pH, dose of coagulant, type of coagulant on COD reduction, and color removal). It was found that only selected factors exhibited a significant effect on the amount of aluminum extracted from red earth. It was also determined that all factors and their interactions exhibited a significant effect on COD reduction and color removal when applying the extracted aluminum in a standard coagulation process. The results were also compared to aluminum sulfate. Furthermore, NaOH was found to be a better extractant of aluminum in red earth than KCl. Therefore, the best extracting conditions for both extractants were as follows: 2 M NaOH and in a 1:5 (soil/volume of extractant) ratio; 1 M KCl and 1:5 ratio. In treating synthetic dye wastewater, the extracted coagulant showed comparable treatment efficiency to the commercial coagulant. The extracted coagulant was able to reduce the COD of the dispersed dye by 85% and to remove 99% of the color of the dispersed dye, whereas the commercial coagulant reduced 90% of the COD and removed 99% of the color of the dispersed dye. Additionally, the extracted coagulant was able to reduce the COD of the reactive dye by 73% and to remove 99% of the color of the reactive dye. However, the commercial coagulant managed to reduce the COD of the reactive dye by 94% and to remove 96% of the color for the reactive dye.

1. Introduction

Dyes are widely used in the textile, leather tanning, paper, food, cosmetics, and colorant industries (Lee et al., 2006). The discharge of dye wastewater into the environment induces both toxicological and esthetical problems as it able to impede light, damage water resources, and make food-chain organisms toxic (Padmesh et al., 2006). The chemical structures of dyes vary enormously, with some having complicated aromatic structures that resist degradation in conventional wastewater treatment processes because of their stability to sunlight, oxidizing agents, and microorganisms (Chu, 2001). In addition, many dyes are toxic to organisms and may cause direct destruction of aquatic communities (Ahmad and Puasa, 2007; Merzouk et al., 2009; Papic et al., 2004).

Among the various wastewater treatment methods, the coagulation–flocculation method is widely applied in the textile industry because of its relative technological simplicity and can even be used as a pre, post or main treatment of wastewater. This process is also cost effective and energy efficient compared to alternative treatments (Papic et al., 2004; Szygula et al., 2009). Chemicals commonly used as coagulants are ferric chloride, ferrous sulfate, polyaluminum chloride, and aluminum sulfate (El Samrani et al., 2004; Georgiou et al., 2003; Tan et al., 2000). These chemical coagulants exhibit different degrees of destabilization where the higher the valence of the counter ion, the more destabilizing effect it exerts, lowering the dose needed (Al-Malack et al., 1999).

Metal coagulants, when dissolved in water, have a tendency to polymerize and form monomeric and polymeric species. Association of such polymeric species onto particles (e.g., dye) creates a coagulant "bridge" that spans between adjacent particles, promoting destabilization. Under appropriate conditions of concentration

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and pH, metal coagulants will form metal hydroxide precipitates, which will serve to enmesh particulates, causing destabilization through a sweeping action (Bratby, 2006). Aluminum and iron salts are commonly used as coagulants in water and wastewater treatment. Their mode of action is generally explained in terms of two distinct mechanisms: i) charge neutralization of negatively charged colloids by cationic hydrolysis products and ii) incorporation of impurities in an amorphous hydroxide precipitate, the so-called sweep flocculation (Ahmad et al., 2008).

A novel source of the above mentioned coagulant is proposed in this work. Therefore, the main objective of this study is to investigate the ability of aluminum extracted from red earth (the novel coagulant) to reduce the COD and to remove the color of Terasil Red R and Cibacron Red R dye solutions (synthetic wastewater) through the coagulation–purification process. Subsequently, the other objective of this study was to compare the efficiency of the aluminum extracted from red earth and commercial coagulant in treating synthetic dye wastewater.

2. Experimental procedure

2.1. Red earth preparation

Red earth was collected from the region of Kulim, in the state of Kedah, Malaysia. The collected red earth was dried in an oven (Memmert, Germany) at 105 °C for 48 h. The dried red earth was then ground into powder using a ball-mill grinder and sieved using a vibrator sieve shaker (Retsch, Germany). This was done to ensure that the particle size was consistent. The processed red earth samples were then stored in a sealed plastic container.

2.2. Characterization of red earth

The prepared red earth sample was characterized using energy dispersive x-ray spectroscopy (EDX) to identify the chemical elements found in the red earth.

2.3. Chemicals

Terasil Red R (CI Disperse Red 324) and Cibacron Red R (FN Reactive Red), both commercial disperse and reactive dyes, were purchased from Ciba (a BASF subsidiary) and used directly without purification to create the synthetic dye wastewater. Properties of Terasil Red R and Cibacron Red R are listed in Table 1. The chemicals $Al_2SO_4 \cdot 16H_2O$ (commercial coagulant) and KCl were obtained from Systerm ChemAR, whereas H_2SO_4 and NaOH were from Merck KGaA and used as extractants and pH adjusters. Distilled water was also used to prepare the synthetic wastewater, the stock solution for the coagulants, and the acid and base solutions.

2.4. Instrumentation and reagents

A HACH DR/2010 spectrophotometer was used to determine the aluminum concentrations, the chemical oxygen demand (COD), and the color point quantification. All reagents involved were analytical grade, and the methods used were according to the protocol of Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Table 1
Properties of aqueous Terasil Red R and Cibacron Red R solutions (average value of 3 samples for dye solutions with concentrations of 300 mg/L).

Parameter	Terasil Red R	Cibacron Red R
Color Index (CI) name	CI Disperse Red 324	FN Reactive Red
Class	Disperse	Reactive
pH	5.65	5.86
COD (mg/L)	665	644
Color measurement (PCU)	10,250	7550

Table 2
Pre- and post-extraction pH of red earth.

Type of soil	Type of solvent used		
	H_2O		
	Test 1	Test 2	Average
Soil (before extraction)	4.10	4.50	4.30
Soil (after extraction)			
Soil extracted with NaOH	10.28	10.16	10.22
Soil extracted with KCl	4.45	4.19	4.32

2.5. Extraction and analysis

Aqueous NaOH and KCl solutions were used as extracting agents on the processed red earth samples. The selection of KCl and NaOH as extracting agents is due to KCl being a common extractant for aluminum whereas NaOH is selected based on its greater dissolution capacity of aluminum from soil. Three factors were studied: 1) the molar concentration of the extracting agent (0.5 M, 1 M, 1.5 M, and 2 M), 2) the ratio of the soil-to-extracting agent (1:5, 1:9, and 1:13), and 3) the type of extracting agent (NaOH and KCl). The duration of the extraction was set at 1 h, and the extracts were separated from suspension by centrifugation at 4000 rpm for 20 min. The extracts were further filtered with cellulose-fiber filter paper with a nominal pore size of 11 μm. The filtrate was analyzed for aluminum using HACH Aluminon Method 8012 with the aid of a spectrophotometer. Finally, the extracted aluminum (aqueous phase) was kept in a polycarbonate reagent bottle at room temperature before further analysis.

2.6. Coagulation

All coagulation experiments were carried out in a standard jar-test apparatus (Velp Scientifica JLT 6) equipped with six stirring rods. Six 500 mL beakers, each filled with 150 mL of dye solution at a dye concentration of 300 mg/L, were used in each run. The pH was varied while other parameters were fixed during the purification process of the synthetic dye wastewater. The pH values chosen for the preliminary runs were 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0. The pH was progressively reduced to identify the best pH for the following runs. The determination of a favorable dose for both coagulants used followed the same steps as the determination of pH, where one of the factors was changed while the other factors were fixed. The dose range chosen for the treatment of the disperse dye was between 350 mg/L and 450 mg/L, whereas for the reactive dye, between 4500 mg/L and 6000 mg/L was used for both the extracted and commercial coagulants. The desired pH was adjusted using 0.1 M H_2SO_4, 0.1 M NaOH, and a pH meter (HACH Sension 1) before adding the extracted and commercial coagulants to the synthetic dye wastewater. The fast mixing speed and duration were fixed at 60 rpm and 1 min, respectively, whereas the slow mixing speed and duration were fixed at 30 rpm and 3 min. The settling time of

Table 3
Chemical elements found in red earth using EDX.

Element	Weight (%)
Aluminum	38.20
Silica	48.14
Iron	13.66

Note: Carbon–oxygen free basis.