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Removal behaviour of a thiazine, an azo and a triarylmethane dyes from polluted kaolinitic soil using electrokinetic remediation technology

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ABSTRACT

In this study, we investigated the potentiality of the electro-kinetic remediation (EKR) technique for the removal of organic dyes polluted soil. Methylene blue (MB), methyl orange (MO), and phenol red (PR) are representing a thiazine, an azo, and a tryarilmethane dye respectively, which was spiked with kaolinite were selected as a model for pollutant dyes tests. An EKR tool (15 cm length) equipped with a DC electric current with the maximum values of 30 V. Graphite electrodes were used for both anode and cathode was set up for two weeks operation. As a result, only 40-55 % of dye was removed from the soil sections by using distilled water. However, by the addition of some electrolytes; the percentage of dyes removed from the soil increased from 73- 76 % and 85 - 89 % for sodium sulphate, and monosodium dihydrogen phosphate, respectively. It resulted that 55-64 % of dyes was removed without controlling the pH. The significant improvement was achieved by controlling the pH of the system. By controlling the pH in the cathode chamber, only 23 % of MB, 25 % of MO, and 18 % of PR dyes remain in the soil sections, respectively. While by controlling the pH in the anode chamber, almost 90 % of tested dyes could be removed from the kaolinite chamber effectively. The movement of a thiazine dye, from the anode to the cathode chamber was controlled by electro-migration and electro-osmosis phenomena. An azo dye transported from the cathode to the anode chamber by a similar process. However, a triarylmethane dye was removed from the soil sections by only electro-osmosis process. For three kinds of tested dyes, it were found that electro-osmotic flow moving from the anode to the cathode directions. The ageing of dye affects the removal percentage of the dye.

1. Introduction

Nowadays, environmental pollution, especially soil pollution has been trending topics and obtaining serious consideration around the world since it appeared as an environmental problem. In terms of soil contamination, there are two kinds of soil contaminant, inorganic contaminants such as, metal and heavy metals, and organic contaminants such as polyaromatic hydrocarbon (PAH), oil, pesticides, and dyes. Dyes are organic colorants used in textile, pharmaceutical, cosmetic, food, and other industries for imparting different shades of colors. As for the textile industries, billion litres of dyes are produced every day around the world. Most of the dye manufacturers and users, particularly in the textile industries, release massive quantities of wastewater containing dye to the extent of 0.001- 0.7 % w/v [1].

Dye wastes, even in low concentrations, are visually detected, affect aquatic life, the food cycle, which become harmful to human health. Methylene Blue (MB), 3,7-bis (Dimethylamino9-phenotiazin-5-ium chloride), $C_{16}H_{18}N_3SCl$ is a thiazine dye which is most commonly used substances for dyeing cotton, wood, and silk. MB give rise to harmful effects for breathing, vomiting, severe headache, diarrhea, painful micturation, and methemeglobinea. Methyl orange (MO), (Sodium 4-[(4-dymethylamino phenylazo)] benzenesulfonate, $C_{14}H_{14}N_3NaO_3S$, is an azo dye. The reductive cleavage of an azo linkage produces aromatic amines which can possibly lead to intestinal cancer. In addition, high concentrations of MO can be dangerous to human life. Phenol Red (PR), also known as Phenolsulfonpthalein, PSP, $C_{19}H_{14}O_6S$, is a tryarilmethane dye attributed with some harmful effects to humans due to the inhibition effect to the growth of renal ephitelial cells. Direct or indirect contact with PR leads to irritations of the eye, respiratory system, and skin. This compound is also toxic to the muscle fibres and has mutagenic effects [2]. Even though there is insufficient records about the real number of victims due to dye pollution, but

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in terms of scientific relevance, this is a great chance to explore and study more on the removal of dye from contaminated soil for environmental safety.

Several methods can be used to remove dyes from the soil through biological, physical, and chemical processes with different advantages and disadvantages of each methods [3–10]. Previous researchers reported about the removal of MB by using carbon derived from peach stones [11], coir pith activated carbon [12], photocatalytic [13], and electrochemical degradation [14]. Even though the application of electro-kinetic remediation has been listed as one of the most promising methods for decontamination of soils polluted from organic and inorganic compounds [15,16]. However, only a few reports of studies on the removal of dyes were found in the literature. Therefore, it is a great opportunity to develop an effective method of soil remediation using cost-effective and eco-friendly technologies for future applications. Electro-kinetic remediation is a method for extracting and removing heavy metal ions and organic pollutants from the soil. This technique allows for the *in situ* removal of contaminants from the soil, so the cost operation and destruction of the soil matrix can be minimized [17]. The application of electro-kinetic remediation for organic and inorganic contaminants has been reported by previous researchers [18–23]..

The basic principle of the electro-kinetic remediation system is the application of low intensity direct voltage or current between anode and cathode through the soil compartment. Contaminants are migrated towards the electrodes by a couple of phenomena. Firstly, by electro-migration process; in which positively charged organic compounds are transported to the cathode sites, and in vice versa, negatively charged organic compounds are migrated to the anode sites. Secondly, by electro-osmosis forces, it was a relative movement of a liquid containing ions with respect to a stationary charged surface [24,25]. During the removal process of organic compounds including dyes in contaminated soil by electro-kinetic remediation, the dye pollutant will be migrated towards the anode or cathode site depending on the charge of the dye.

This study demonstrated the trend and behaviour of the removal of three dyes from polluted soils by EKR. Since the results significantly depends on the operating conditions and the chemical structure of the dyes, thus several parameters such as, pH, the initial concentration of dye, the addition of electrolyte into the system, and ageing effect of the dye in the soil were investigated. The transportation and the distribution of pollutant dyes and the directions of electro-osmotic flow for each dye after EKR process was also studied.

2. Experimental

2.1. Materials

Kaolinite clay soil used in this study with the the precipitation volume of 4.0–6.5 ml/g

was obtained from Wako Pure Chemical Industries, Ltd., Japan. The soil contains 82 % of clay and 18 % of silt. A thiazine dye (MB) was purchased from Kanto Chemical Co. Inc., Japan, while an azo dye (MO), a triarylmethane dye (PR), sodium sulphate, and monosodium dyhidrogen phosphate were purchased from Wako Pure Chemical Industries, Ltd., Japan.

2.2. Kaolinite sample preparation

Polluted kaolinite samples in this study were prepared by the mixing process. One hundred and twenty grams of kaolinite clay minerals were mixed with 40 ml of MB, MO, or PR 300 mgL^{-1} dyes solution thoroughly, and a mixture of 100 mg dye/kg dry kaolinite was obtained. The mixture stands up for 24 h for the drying procedure. The molecular structure of dyes are shown in Fig. 1. The initial pH of the mixtures was around 4.1-4.3, and the moisture content of the mixtures was around 32 % in all experiments. Kaolinite clay mineral was selected as a model of soil matrix due to the suitable parameters such as lower buffering capacity, and cation exchange capacity compared with other clay minerals [26].

2.3. Electro-kinetic Remediation (EKR) Cell

The EKR system used in this study was set up as shown in Fig. 2. It consists of a soil compartment, two electrode chambers, a peristaltic pump, a power supply and a data recorder. Graphite electrodes with the length of 8-10 cm and a diameter of 4-6 mm were purchased from CZ Republic and were used for both the anode and cathode. The sample, 120 g of dyes polluted kaolinite was loaded to the soil chambers.

The processing fluid or electrolyte was inserted to the electrode chamber solution to enhance the electrical conductivity of the

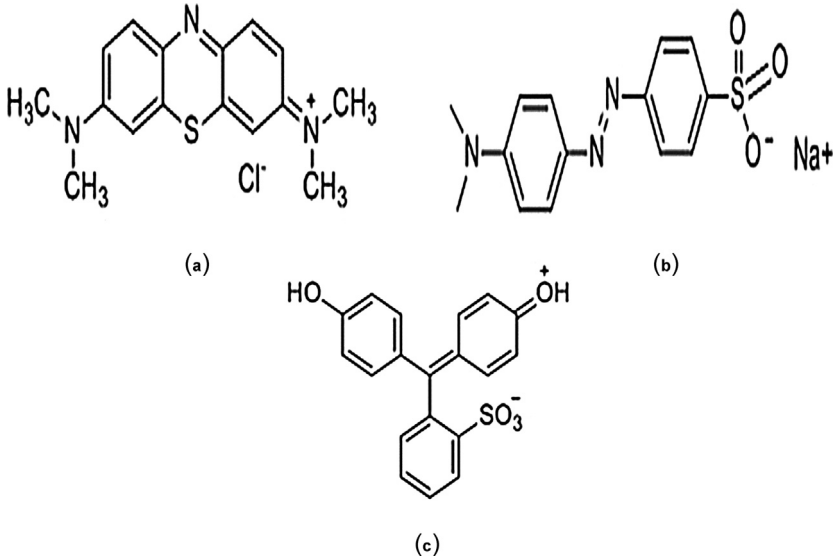

Fig. 1. Chemical structure of tested dyes (a) methylene blue, C16H18N3SCl, (a thiazine dye), (b) methyl orange, C14H14N3NaO3S (an azo dye), and (c) phenol red C19H14O5S, (a triarylmethane dye).