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Water treatment process intensification by combination of electrochemical and photochemical methods

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ABSTRACT

Wastewater contamination is typically characterized by a combination of organic and inorganic compounds rendering treatment relying on a single treatment approach almost always unfeasible. The treatment of complex waste matrices not only poses the process challenge of reducing the concentration of a number of contaminants to safe levels but also achieving it through an efficient, affordable and simple process. A key challenge in achieving this is the identification of techniques that operate symbiotically to: enhance the performance of the system as a whole and; reduce the number of process steps. Here such process symbiosis is presented, through the treatment of a model effluent containing iron and nitrobenzene, by electro-coagulation (EC) and photooxidation (PO), individually and in combination. It was found that the combination of two techniques, which individually were unable to completely remove contamination, achieved 100% contaminant removal in a shorter reaction time and consuming less H_2O_2.

1. Introduction

Massive industrial development and environment unfriendly waste disposal practices have led to non-negligible soil and groundwater contamination in many locations around the globe. Heavy contamination of subsurface suburban waters caused by a wide variety of organic and inorganic compounds can be typically found in the environment surrounding many former chemical plants in Central and Eastern Europe. The requirement for comprehensive decontamination of such areas is obvious and conventional approaches, such as biodegradation or sorption, are not always effective given the mixture of organic and inorganic compounds present, the latter typically as dissolved metallic ions.

There is, therefore, a requirement for robust technology and methodology that is capable of tackling complex matrices of contamination. Furthermore, given the scale and dispersion of contaminated sites, treatment should preferably be carried out in situ. This not only avoids the economic and environmental cost of transporting large volumes of soil and water over long distances, but also reduces the risk of further contamination.

Enabling such low risk and effective approaches require development of technology that is compact (for ease of transportation) and effective over a broad range of contaminants (for simplicity of operation). The work presented here combines electrochemical and photochemical methods to meet such requirements.

In this methodology, influent streams were initially treated by electro-coagulation (EC), principally for effective removal of inorganic contamination [1–5], followed by photochemical degradation of the residual organic contamination employing UV-C and hydrogen peroxide. It has also been pointed that electro-coagulation may effectively contribute to the partial removal of organic compounds [6–8].

Electro-coagulation is based on the electrochemical dissolution of “sacrificial” electrodes (typically steel or aluminium [9]) and formation of solid porous particles (hydroxides) which (ad) absorb suspended matter and dissolved inorganic ions. More detailed information regarding the mechanisms on electro-coagulation and ongoing electrochemical reactions can be found elsewhere [10–13].

Despite its applicability in water treatment, iron can be commonly found both as a natural contaminant in ground- or wastewaters, and as a consequence of industrial development (metal corrosion of chemical apparatus, iron and steel industry, mining) [14], mainly in the form of ferrous(II) and ferric(III) ions. Iron removal can be performed by several techniques, e.g., ion exchange and water softening, oxidation by aeration and chlorination followed by filtration through activated carbon, and other filtering materials [15–18]. Supercritical fluid extraction,

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Nomenclature

c_A	Concentration of reactant (mmol/L)
t	Reaction time
c_{A0}	Initial concentration of reactant (mmol/L)
k	Rate constant (s^{-1})
n	Order of reaction
EC	Electro-coagulation
FTL	Flow-through-loops number
PO	Photooxidation

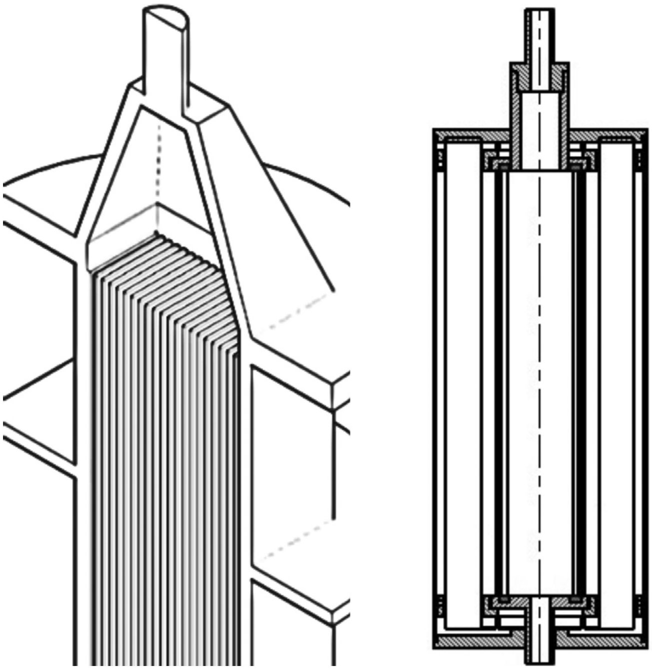

Fig. 1. Left – EC cell interior scheme; right – UV reactor interior.

limestone treatment or bioremediation can be also applied [19,20]. Among other methods standard chemical coagulation and electro-coagulation can be applied. In this study, iron (in the form of steel) was employed as a coagulant for its wide availability, low cost and low toxicity.

For total organic compounds removal, chemical oxidation techniques often are well suited and significant effort has been committed to the research of photocatalytic oxidation with titanium dioxide or to the $H_2O_2/Fe^{2+}(Fe^{3+})$/UV processes [21–23]. A much simpler option for organics decomposition uses highly reactive radicals produced by interaction of the UV-C light with H_2O_2. The UV-C/H_2O_2 system is based on the decomposition of hydrogen peroxide towards hydroxyl radicals using ultraviolet irradiation with wavelengths below 280 nm [24]. The mechanism of hydroxyl radical formation is understood as homolytic cleavage of hydrogen peroxide molecule yielding two radicals. More details on the mechanism of hydrogen peroxide decomposition can be found elsewhere [25–27].

The work presented below stems from research carried out to improve the knowledge regarding these processes and develop a deeper understanding of its limitations and capabilities.

2. Experimental

As mentioned above, electro-coagulation was primarily employed for the removal of inorganic contaminants (although it also contributed to the removal of organics) whilst the photochemical process was employed for the removal of the organic component of the contamination. Both methods can be tested separately or in a series but, when used in series, electro-coagulation must operate as a pre-treatment step to prevent fouling of the photoreactor and enable efficient operation.

2.1. Chemicals

$FeCl_3{\cdot}6H_2O$ (per analysis quality, Sigma–Aldrich) was chosen as a model pollutant representing inorganic contamination. Nitrobenzene (per analysis quality, Sigma–Aldrich) was chosen as model organic contaminant, and hydrogen peroxide (unstabilized 29–32%, Lach-Ner) was used for oxidation reactions. The selection of nitrobenzene and iron contaminants reflected practical needs of industrial project partners.

2.2. Reactor assembly

2.2.1. Electro-coagulation

A closed reactor (inner dimensions 250 × 55 × 55 mm) supporting vertically mounted mild steel electrodes (210 × 55 × 1 mm) connected to a 16 V/10 A regulated power supply (EA-PS 2016-100) was used (Fig. 1). The experimental arrangement allowed working either in flow-through or recirculation mode to suit testing requirements whilst the EC cell accommodated up to five anodes and cathodes. The reported experiments were carried out in flow-through mode, and one anode and one cathode were used (active electrode surface was 115.5 cm^2), with all other positions blocked such that a 6 mm inter-electrode channel was left open.

2.2.2. Photochemical oxidation

An in-house reactor design was developed where a quartz tube (290 mm long, 50 mm inner diameter) was surrounded with 12 germicidal low-pressure UV lamps with maximum emission at 254 nm (Philips, LT 8W UV-C, 12 × 145 mW/cm^2) (Fig. 2).

The quartz tube is an essential element of the photochemical system, protecting the UV lamps from solution whilst enabling UV-C radiation to effectively travel through bulk solution. However, quartz is sensitive to inorganic ions and can selectively adsorb them [28,29] leading to fouling of the surface and hence loss of performance. The reactor outer jackets are made of highly polished aluminium sheet to ensure maximum light reflectance including lengthwise sheets operating as heat sinks.

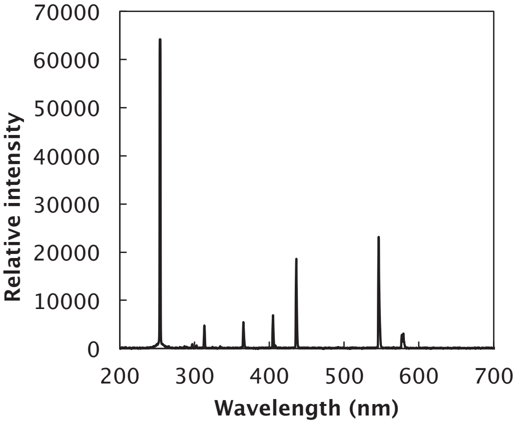

Fig. 2. Emission spectrum of low pressure germicidal UV lamps.