

Combined Effects of Surfactant-Assisted Soil Washing and the Electro-Fenton Process on Fluorene Removal

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Soil washing has been widely used together with other remediation techniques to increase the overall removal efficiency of hydrophobic pollutants. In this study, the combined effects of soil washing followed by the electro-Fenton process were investigated. A loamy soil contaminated with fluorene (368.8 mg/kg) was used in a washing process including the non-ionic surfactant polyoxyethylene 20 cetyl ether (Brij 58). A total of 222.6 mg/kg fluorene was removed with 1% Brij 58 solution and a soil-to-solution ratio of 1/5, which were determined to be the optimum treatment conditions. Both the first-order, two-compartment model and pseudo-second-order model described fluorene solubilization very well, implying that fluorene solubilization proceeded in two stages and that the fluorene concentration gradient in the washing solution influenced the process. Evaluation of Brij 58 adsorption together with fluorene removal revealed that adsorption and the release of organic constituents (Brij 58 and dissolved soil organic constituents) and fluorene from the soil seemed to occur simultaneously. The treatment of the Brij washing solution with the electro-Fenton process presented a fluorene removal efficiency of approximately 92.8% with 2% H₂O₂ and a reaction time of 60 min, a current density of 15 mA/cm² and an electrical conductivity of 2 mS/cm. The corresponding total destruction of the washing solution was approximately 67.6%. The results showed that with proper optimization of operational parameters, a strategy for the removal of target contaminants can be accomplished, enabling the reuse of the washing solution.

Keywords: Fluorene, Combined Soil Remediation, Surfactant, Electro-Fenton Oxidation

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic compounds naturally and anthropogenically originating from incomplete combustion during wildfires and

combustion activities. Major PAH sources have been determined as point sources, such as power plants and aluminium smelters, rather than non-point sources [1-3]. Due to their mutagenic, teratogenic and carcinogenic characteristics, PAHs have been extensively studied [4], and among them, 16 PAHs have been determined as priority pollutants by the European Commission (EC) and the US Environmental Protection Agency (USEPA) [5]. The partitioning of PAHs in the environment occurs mainly between air and soil with respect to their molecular weight (number of benzene rings), structure and other physicochemical properties [1,6,7]. The soil eventually ends up being the major environmental sink for PAHs due to their high affinity for soil components such as soil organic matter and their high hydrophobicity [8].

The number of polluted sites in Europe is estimated to be 250,000 [9]. Approximately 13% of the pollutants affecting the soil and groundwater are estimated to be PAHs [9]. Like any other toxic contaminant in the soil, the cleanup of PAH source zones will reduce their mobility and thus their exposure pathways. Among various physicochemical and biological remediation technologies, soil washing is generally accepted as a simple and economically feasible technology for the remediation of polluted soils [10,11]. Soil washing generally employs extractants such as surfactants, organic and inorganic complexing agents and other solvents for the desorption of PAHs from polluted soils. The solubilized PAHs in the washing solution require treatment after desorption [12]. Therefore, the combination of soil washing with other cleanup technologies involving physicochemical, physical-biological or physicochemical-biological processes is often preferred. This approach also overcomes the unavailability problem of non-aqueous phase liquids (NAPLs) and increases the removal efficiency [13-15].

The combination of soil washing and chemical oxidation is often used for increasing PAH removal efficiency [14,16]. This combined process is named surfactant-enhanced or surfactant-assisted chemical oxidation. Chemical oxidation relies on electron transfer between an oxidant and the pollutants during the conventional redox reaction. Under catalytic conditions, powerful free radical oxidant systems prevail, leading to the so-called advanced oxidation process (AOP). AOPs involve the generation of non-selective radicals (e.g., hydroxyl ($\bullet\text{OH}$) and sulphate ($\bullet\text{SO}_4$) radicals) with the canalization of hydrogen peroxide (H_2O_2), ozone (O_3), and persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) oxidants, among others, under favourable pH and temperature conditions and/or the presence of transition metals [17].

Hydrogen peroxide is one of the most widely used oxidant in soil remediation [14]. Ferrous iron (e.g., $\text{Fe}(\text{SO}_4)$, other salts of $\text{Fe}(\text{II})$ or chelated $\text{Fe}(\text{II})$) has been used for the activation of hydrogen peroxide to generate hydroxyl radicals ($E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$), leading to the Fenton process. In homogeneous Fenton process studies, iron is added externally by simultaneous injection/addition of a dissolved ferrous iron solution. Ferrous iron can also be produced during the Fenton process by electro-generation from iron anodes. This combined process is called the electro-Fenton (E-Fenton) process [18]. The E-Fenton process is generally accepted as environmentally friendly, as harmful chemicals are not consumed and the use of electricity from sustainable energy sources is possible.

Regarding the combination of soil washing with the E-Fenton process, several studies have been carried out using different surfactants and electrodes. Among these studies, Mousset et al. [19] used hydroxypropyl-beta-cyclodextrin (HDCD) and Tween 80 (TW 80) surfactant solutions to remove six PAHs with varying ring numbers (acenaphthene, phenanthrene, fluoranthene, pyrene,

benzo(a)pyrene and benzo(g,h,i)perylene), which were treated with Fenton's reagent. The results showed that higher removal efficiencies were obtained for PAHs with relatively lower ring numbers than for those with higher ring numbers with the addition of Tween 80. Complete PAH degradation (>99%) was achieved twice as quickly with HDCD (4 h) than with Tween (8 h). Trellu et al. [20] applied an AOP using a boron-doped diamond anode for the destruction of phenanthrene, anthracene, pyrene and fluoranthene and found that the current density and surfactant concentration highly influenced the degradation efficiency. It was explained that the selective destruction of target compounds can be obtained by using a low current density and high surfactant concentration. Sandu et al. [21] studied historically contaminated sites and presented that use of the surfactants Tween 80 and Triton X100 improved contaminant solubilization and the electroosmotic flow of H₂O₂, enabling higher removal efficiencies.

Referring to previous Fenton oxidation studies, there have been few studies conducted on the enhancement of PAH removal with both surfactant use and electro-kinetics. Fluorene was selected as the model compound of the 16 priority PAHs that have not been studied in a combined soil washing and E-Fenton oxidation process. The objective of this study was to investigate the efficacy of the combined remediation process by initially determining the optimum conditions of the washing process (e.g., time, Brij 58 concentration and soil-to-solution ratio). As the second step, destructive removal of fluorene was examined by monitoring the influence of reaction time, current density and electrical conductivity on the E-Fenton process. Optimum treatment conditions were determined by monitoring fluorene and COD removal efficiencies.

2. MATERIAL AND METHOD

2.1. Chemicals

The surfactant Brij 58 (C₁₆H₃₃(OCH₂CH₂)₂₀-OH) was provided by Sigma-Aldrich and was of analytical grade. Fluorene (C₁₃H₁₀) with a purity of 95% was purchased from MERCK. HPLC-grade (>99.9%) acetonitrile (CH₃CN), acetone (CH₃COCH₃) and hexane (C₆H₁₂) were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂) with a purity of 30% was supplied by MERCK. All other chemicals (FeSO₄×7H₂O, K₂Cr₂O₇, H₂SO₄, AgSO₄, HgSO₄, Na₂SO₄ and NaOH) were of ACS reagent grade. Finisterre SPE cartridges (TR-F034084) were used for solid-phase extraction.

2.2. Preparation of spiked soil

A topsoil sample (0-20 cm) was taken for an earlier soil survey study from the Carsamba Plain of Samsun. The physicochemical properties were determined according to standard procedures. The texture was determined using the ASTM D 422-63 method [22]. Soil pH was determined according to ASTM D 4972-95a using a Sartorius PB 20 pH meter [23]. The carbonate content was measured using a Scheibler calcimeter [24]. Organic matter analysis was carried out according to TS 8336, which is a Walkey-Black-based method from the Turkish Standards Institute [25]. The cation exchange capacity

(CEC) of the soil was analysed as described by Rump and Krist [26]. The soil was characterized as a loamy soil with 26.9% clay, 46.4% silt and 26.7% sand. The main soil properties were found as follows: pH, 7.3; carbonate content, 4.8%; organic matter content, 2%; and CEC, 175 meq/100 g.

The soil was homogeneously contaminated by mixing the soil with fluorene, which was previously dissolved in hexane, to yield an approximate fluorene concentration of 500 mg/kg in soil. This concentration was chosen to resemble the typical PAH concentration found near source zones of contaminated sites [27]. The soil-fluorene-hexane mixture was placed within a ventilation hood at room temperature ($20\pm 2^\circ\text{C}$) for 10 days until the hexane had completely evaporated. Afterwards, the soil was stored in the dark at $+4^\circ\text{C}$ to avoid biodegradation. The exact concentration of fluorene was measured since some fluorene might have volatilized along with the solvent [28].

2.3. Soil washing experiments

Brij 58, a non-ionic surfactant, was selected as the model surfactant in this study, as it has rarely been reported in the literature. The Brij 58 solution was prepared by dissolving an appropriate amount of surfactant in distilled water to achieve concentrations higher than its critical micelle concentration, which is 0.0086% or 7.7×10^{-2} mM ($20\text{-}25^\circ\text{C}$). The washing process was carried out as a series of batch experiments to determine the optimum time, surfactant concentration and soil-to-solution ratio. The experiments were carried out in 250 mL Erlenmeyer flasks with caps. Pre-determined amounts of contaminated soil and surfactant solution were placed into the flask and stirred at a rate of 150 rpm at room temperature in a water bath shaker. Before use, all flasks were cleaned with acetone (>99.9%) and then rinsed several times with distilled/deionized water to avoid cross-contamination. The suspensions were centrifuged to obtain the supernatant for fluorene determination.

In the kinetic study, the reaction time varied between 30 min and 2880 min at a surfactant concentration of 1% and a soil-to-surfactant solution ratio of 1/10. The subsequent set of experiments was carried out to determine the influence of surfactant concentration (0.5%, 1%, 2% and 5%) on removal efficiency. In these experiments, a reaction time of 1440 min and a soil-to-solution ratio of 1/10 were chosen. The effect of the soil-to-surfactant solution ratio (1/2-1/20) was examined in experiments where fluorene-contaminated soil interacted with Brij 58 (1% and 5%) for 1440 min.

2.4. E-Fenton oxidation treatments

The fluorene-containing Brij 58 solution used in the E-Fenton oxidation experiments was prepared according to the results of the optimum washing process conditions. The oxidation experiments were conducted in a 1 L cubic Plexiglas cell containing six $4.5\text{ cm} \times 7.5\text{ cm}$ sized iron plates. The electrodes were connected to a digital direct current (DC) power supply (GW GPC-3060D) in a particular sequence to support three anode and three cathode electrodes consecutively placed into the cell (Fig. 1). The distance between the electrodes was 0.9 cm. Before each run, the electrodes were initially rinsed with acetone to remove grease and then dipped into an aqueous solution composed of 100 mL of HCl (35%) and 200 mL of hexamethylenetetramine (2.80%) for 5 min [29]. The E-Fenton

oxidation experiments were carried out with 900 mL of washing solution that was placed into the electrolytic cell. Solid sodium sulphate was added to increase the conductivity of the medium. After current density adjustment and H₂O₂ addition, the E-Fenton process was initialized by decreasing the pH to approximately 3.5. The reaction was terminated by decreasing the pH below 1 using 1 M H₂SO₄. Cooling was applied to maintain the temperature at approximately 25°C. After treatment, separation was achieved by centrifugation at 2000 rpm. After each run, electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried, and weighed again.

Initial experiments were conducted with 2% H₂O₂, a current density of 15 mA/cm² and conductivity of 6 mS/cm to determine the influence of time (15-120 min) on removal efficiency. To examine the influence of current density (5-20 mA/cm²), experiments were repeated under identical conditions (2% H₂O₂ and 6 mS/cm) for the determined optimum time period. Similarly, the effect of conductivity (2-18 mS/cm) was monitored by conducting E-Fenton experiments with 2% H₂O₂ for the optimum time. The influence of H₂O₂ concentration (0.5%, 1%, %2 and %5) was studied under optimized conditions. Most experiments were carried out in triplicate and at room temperature (25±2°C).

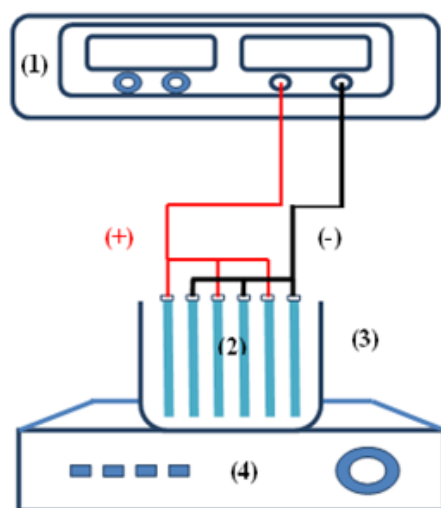


Figure 1. Experimental set-up: (1) DC power supply, (2) electrode pair, (3) electrolytic cell and (4) magnetic stirrer.

2.5. Analytical procedures

Before and after treatment, the fluorene (FLU) in the spiked soil samples was extracted according to the USEPA Test Method 3540C using a Soxhlet apparatus [30]. The soil samples, which were mixed with anhydrous Na₂SO₄, were transferred into Whatman cellulose extraction thimbles (43×123 mm) dipped in solvent for at least 24 h before use. The extraction was carried out with a hexane and acetone mixture (50:50 v:v) for 24 h at a rate of 4-6 cycles/h.

Solid-phase extraction (SPE) was applied to all samples before chromatographic analysis [31]. For this purpose, floroil-filled 1000 mg/6 mL SPE cartridges were used. After the conditioning of

SPE cartridges with 5 mL of n-hexane, 5 mL of sample was passed through each cartridge on a vacuum manifold at a speed of 1 mL/min to enable the target material to be adsorbed to the solid phase in the cartridge. Using 5 mL of acetonitrile, the fluorene was eluted from the cartridge to the filtrate, which was concentrated under the nitrogen gas up to 1 mL. The concentrated samples were passed through 13 mm 0.22 μm PVDF syringe disk filters before chromatographic analysis.

Fluorene was analysed with an HPLC (Shimadzu LC-20A Prominence) instrument coupled with an ultraviolet diode array detector (UV-DAD) and a Pinnacle®II reverse-phase column (250 mm \times 4.6 mm i.d., 4 μm). The injection volume was chosen to be 5 μL , and the isocratic eluent (60:40 acetonitrile/water) was pumped at a rate of 0.5 mL/min for 35 min [32]. The column temperature was kept constant at 20⁰C and the effluent flux was set at a constant rate of 1.5 mL/min. After the injection of fluorene into the HPLC, the retention time, the limit of detection (LOD) and the limit of quantification (LOQ) of fluorene were determined to be 15.205 min, 0.296 ng/mL and 0.896 ng/mL, respectively. The correlation coefficient of the calibration curve was found to be 0.9999. Sample preparations and analyses were carried out at the Department of Pharmacology and Toxicology of Veterinary Faculty at Ondokuz Mayıs University.

The efficiency of each process was additionally interpreted by following the changes in the overall organic matter content of washing solutions (e.g., soil organic matter, fluorene and surfactant) measured as the chemical oxygen demand (COD) of untreated and treated solutions. COD analyses were carried out according to the closed reflux method [33]. Two millilitres of a sample solution was added to a COD cell that contained 1.5 mL of K₂CrO₇ digestion solution and 2.5 mL of acid solution. The COD cell was incubated in a MERCK TR 620 thermoreactor for 2 h at a temperature of 148°C and analysed at 605 nm using a Spectroquant NOVA 60 photometer.

The iron concentration in the washing solutions was measured with flame atomic absorption spectrometry (AAS) using a Unicam 929 AA spectrophotometer equipped with a deuterium background corrector.

2.6. Data analysis

2.6.1. Performance

The performance of the washing process was calculated using Eq. (1), where q is the amount (mg/kg) of fluorene initially measured in the contaminated soil, q_t is the amount (mg/kg) of fluorene desorbed from the soil at time (t) calculated from the fluorene concentration (C_0) in washing solution [Eq. (2)], V is the volume (L) of washing solution, and M is the amount (kg) of soil used in the washing process.

$$\text{Removal Efficiency (\%)} = \frac{q_t}{q} \times 100 \quad (1)$$

$$q_t = \frac{V \times C_0}{M} * 1000 \quad (2)$$

The treatment performance of the E-Fenton process was evaluated by calculating the fluorene and COD removal efficiencies according to Eq. (3), where C_0 represents the initial concentration (mg/L) in the washing solution before oxidation and C_t is the residual concentration at reaction time t (min). The results are presented as the average of three independent measurements.

$$\text{Removal Efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} * 100 \quad (3)$$

2.6.2. Kinetics

2.6.2.1. Kinetics of the washing process

A kinetic evaluation to understand the solubilization of fluorene from soil during the washing process was carried out. The solubilization of fluorene was interpreted by fitting the data to the pseudo-first order [Eq. (4)] and second-order rate models [Eq. (5)] [34,35].

$$\frac{d[q_t]}{d[t]} = -k_1 [q_e - q_t][\text{Brij58}] \rightarrow \frac{d[q_t]}{d[t]} = -k_1 [q_e - q_t] \quad (4)$$

$$\frac{d[q_t]}{d[t]} = -k_1 [q_e - q_t]^2[\text{Brij58}] \rightarrow \frac{d[q_t]}{d[t]} = -k_1 [q_e - q_t]^2 \quad (5)$$

Because Brij 58 concentrations [Brij 58] were above CMC and thus abundant in solution, the second-order rate equation became pseudo-first order [Eq. (4)], and the third-order rate equation became pseudo-second order [Eq. (5)]. After integration, Eq. (4) became Eq. (6), and Eq. (5) became Eq. (7).

$$\ln[q_e - q_t] = \ln[q_e] - k_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 * q_e^2} \quad (7)$$

where q_e is the amount (mg/kg) of fluorene released from the contaminated soil at equilibrium. Linearized plots of $\ln(q_e - q_t)$ versus time (t) and (t/q_t) versus t yielded the first-order and second-order rate constants k_1 (1/min) and k_2 (kg/mg·min) from the slope and intercept, respectively.

The desorption kinetics of aromatic hydrocarbons from soil and sediment are often explained by the first-order two-compartment model [36-38], as the process is assumed to occur with an initial fast release followed by a much slower, long-term release [Eq. (8) and Eq. (9)]. In this equation, f is the rapidly desorbing fluorene fraction.

$$q = f * q_{fast} + (1 - f) * q_{slow} \quad (8)$$

$$q_t = q_e [1 - (f * e^{-k_{fast} * t} + (1 - f) * e^{-k_{slow} * t})] \quad (9)$$

2.6.2.2. Kinetics of the oxidation process

The pseudo-first-order rate model has generally been used for the kinetic evaluation of the Fenton or E-Fenton process in most studies. However, good correlations for the pseudo-second-order rate model were also published. Thus, both kinetic models were used, assuming the main oxidation reaction of organic compounds (e.g., FLU) to be as follows:



$$\frac{d[C]}{d[t]} = -k_1 [C][\text{OH}^{\bullet}] \rightarrow \frac{d[C]}{d[t]} = -k_1 [C] \quad (10)$$

Assuming that the primary radical of the Fenton process $[\text{OH}^{\bullet}]$ is continuously produced in solution and thus present in excess concentrations, the second-order rate equation [Eq. (10)] became pseudo-first order. Eq. (10) became Eq. (11) after integration, yielding a linearized plot of $\ln(C_t/C_0)$ versus time, where C_0 is the initial organic compound concentration (e.g., FLU) and C_t is the concentration observed at time t .

$$\ln[C_t] = \ln[C_0] - k_1 t \quad (11)$$

Regarding the third-order rate equation [Eq. (12)], a pseudo-second-order rate equation was similarly obtained.

$$\frac{d[C]}{d[t]} = -k_2 [C]^2[\text{OH}^{\bullet}] \rightarrow \frac{d[C]}{d[t]} = -k_2 [C]^2 \quad (12)$$

Eq. (12) became Eq. (13) after integration, yielding a linearized plot of $[(1/C_t) - (1/C_0)]$ versus time.

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \quad (13)$$

3. RESULTS AND DISCUSSION

3.1. Fluorene concentration in contaminated soil

Within the scope of the project, studies were carried out as series of batch experiments. The fluorene concentration measured in the polluted soil samples that were used for the E-Fenton study was 368.8 mg/kg. The lower fluorene concentrations were related to volatilization of fluorene during hexane evaporation and adsorption of fluorene onto glassware during the contamination study [28,39].

3.2. Fluorene solubilization with Brij 58

Brij 58, a non-ionic surfactant, was selected as the model surfactant in this study, as it has rarely been reported in the literature. Non-ionic surfactants are generally known for their elevated solubilization performance and lower cost compared with cationic and anionic surfactants [40,41].

3.2.1. The influence of washing time on fluorene solubilization

The influence of washing time on fluorene removal from soil was examined using an average Brij 58 concentration of 1% and a soil-to-solution ratio of 1/10. The results in Fig. 2 indicate an initial fast fluorene removal of 192.56 mg/kg within 120 min, which continued to increase and reached values of 222.57 mg/kg and 237.00 mg/kg within 1440 min and 2880 min, respectively, and the corresponding removal efficiencies were determined to be 60.34% and 64.26%, respectively. The optimum washing time was chosen to be 1440 min. Amir et al. [34] similarly suggested 24 h as the cost-effective contact time for soil washing.

The washing process was evaluated using pseudo-first-; first-order two-compartment; and pseudo-second-order kinetic models. The kinetic model parameters (e.g., rate constants) and correlation coefficients are presented in Table 1. The correlation coefficient was lowest for the pseudo-first-order equation ($r^2=0.802$). The coefficients ($r^2\geq 0.994$) observed for the first-order two-compartment model were higher than those of the other models, implying that fluorene solubilization proceeded in two stages. The rate of fast release ($k_{\text{fast}}=0.00709 \text{ min}^{-1}$) was found to be tenfold higher than the rate of the slower second stage ($k_{\text{slow}}=0.00069 \text{ min}^{-1}$). It was explained that the PAHs that are close to the surface are solubilized faster, while the release of deeply bound PAHs is controlled by diffusion through intraparticle micropores and nanopores [34,42]. Regarding the rate constants, k_{fast} was in agreement with the data published by Barnier et al. [37] for other PAH compounds; however, k_{slow} seemed slightly higher than previously reported values, which might be attributed to the adsorption-desorption behaviour of fluorene [43,44]. The solubilization of two-three aromatic ring (lighter) PAHs is known to be higher than that of heavier PAHs due to their lower octanol-water partition coefficients [36,37].

Table 1. Parameters and correlation coefficients of kinetic models

Kinetic Models	k_1^* (1/min), k_2^{**} (kg/g·min)	k_{fast} (1/min)	k_{slow} (1/min)	f	r^2
Pseudo-first order two compartment model	-	0.00709	0.00069	0.81	0.994 (fast) 0.993 (slow)
Pseudo-first order*	0.00108	-	-	-	0.802
Pseudo-second order**	0.00011	-	-	-	0.999

The correlation coefficient was highest for the pseudo-second-order equation ($r^2=0.999$), indicating the importance of the fluorene concentration gradient in the washing solution. Hu and

Aitken [45] stated that as contaminants in soil layers near the hydrophobic surface are depleted, the concentration gradient serves as a driving force for the contaminants to diffuse from the soil layers to the hydrophobic surface. Phenanthrene desorption by surfactants (Triton X-100, Tween 80, etc.) was also well explained with the pseudo-second-order model by Amir et al. [34] and Wang et al. [46]. The calculated rate constant (0.00011 kg/mg·min) was in accordance with the values reported by Amir et al. [34]. The q_e value (237.64 mg/kg) calculated from the linearized form of the pseudo-second-order equation was found to be the closest to the value (237 mg/kg) observed for the 2880th minute of experimental study.

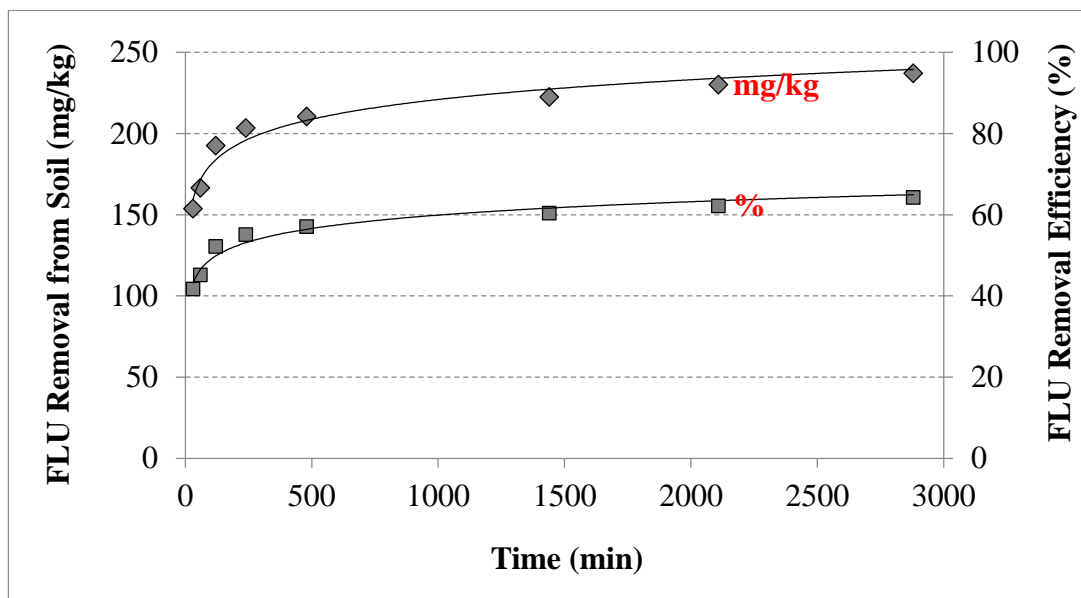


Figure 2. The influence of washing time on fluorene removal with 1% Brij 58 solution (soil/solution: 1/10).

Regarding the change in COD concentrations with time, a similar increasing trend was observed, rising from 11700 mg/L to 13325 mg/L at the end of treatment time (Fig. 3). This increase was related to both the removal of fluorene and the dissolution of soil organic matter from soil. The sorption of PAHs is known to mainly occur by soil organic matter (SOM), as was similarly reported for fluorene [43,47,48]. Additionally, the reversibility of sorption by SOM is expected to be higher for PAHs with relatively lower octanol-water partition coefficients than for those with higher partition coefficients. The rate of sorption-desorption and hysteresis was attributed to the amount and characteristics of organic matter found in soil [43]. The influence of dissolvable SOM was also found to play an important role in soil contaminant interactions [49], as was observed in this study.

As shown in Fig. 3, the initial COD concentration of the prepared 1% Brij solution was determined to be 14562.30 mg/L. Therefore, the adsorption of 1% Brij 58 was investigated with respect to time to understand the on-going processes during the interaction of the washing solution with the soil. Thus, additional adsorption experiments were carried out under identical experimental conditions using uncontaminated soil. The change in COD concentrations after the interaction of 1% Brij washing solution with soil at a soil-to-solution ratio of 1/10 can be seen in Fig. 3 and Fig. 4. The

COD concentration decreased from 14562.30 mg/L to 12400 mg/L and to 9547 mg/L at the end of 120 min and 2880 min, respectively. Thus, as the COD concentration of the Brij 58 solution decreased, the adsorption of Brij 58 increased, yielding values of 33.13×10^3 mg/kg (22.7%) and 50.16×10^3 mg/kg (34.4%), respectively. The adsorption of non-ionic surfactants and especially cationic surfactants, is well known [50,51]. The adsorption of surfactants generally relies on hydrophobic interactions and is therefore expected to increase with increased SOM content [52]. Non-ionic surfactants were also reported to bind to soil surfaces with hydrogen bonding on the -OH sites of soil, in addition to hydrophobic interactions [53]. However, the interaction of nonpolar surfactants with organic compounds is underlined for soils with a relatively high organic content [54]. Among the many surfactants, Brij 30 and Brij 35 were found to adsorb on soil at much lower levels, when compared with Tween 40 and Tween 80, resulting in higher phenanthrene removal efficiencies [51]. Brij 58 was found to have a lower sorption affinity towards soil than Brij 30 due to its longer chain [55]. The hydrophilic lipophilic balance (HLB) values of these two surfactants ($HLB_{Brij58}= 15.5$ and $HLB_{Brij30}=9.7$) support this finding [56].

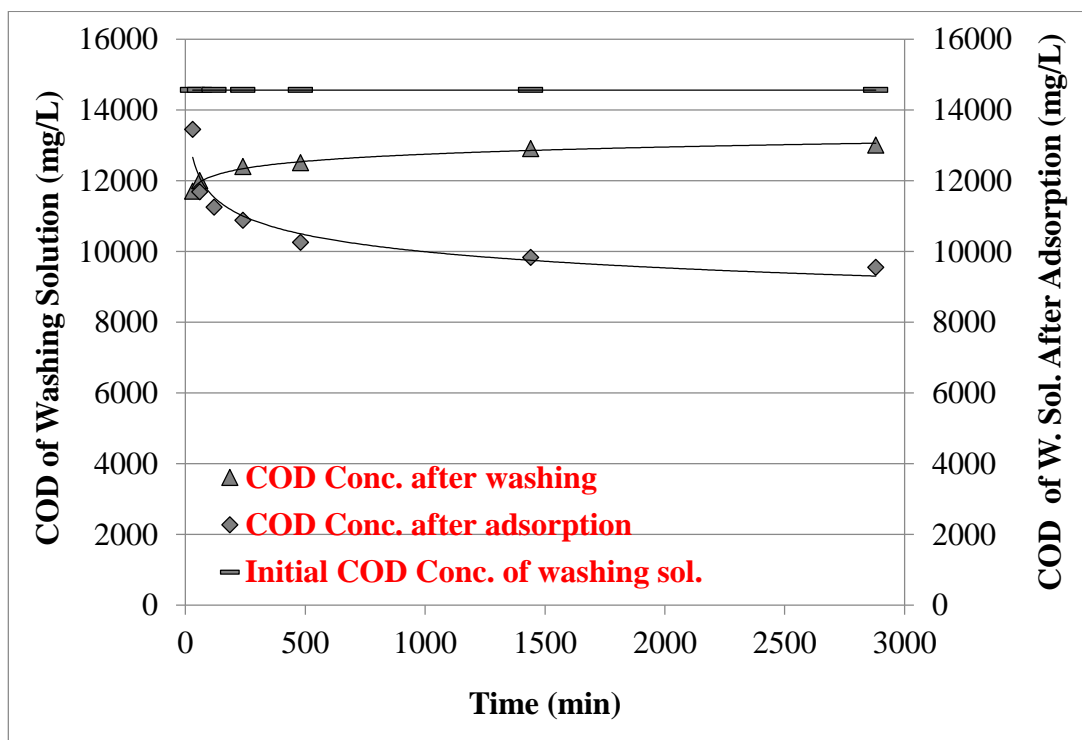


Figure 3. The influence of time on the COD concentration of the 1% Brij 58 solution after washing and adsorption processes (soil/solution: 1/10).

Regarding the amounts of surfactant adsorbed, Ahn et al. [51] reported lower values than those observed in this study, which was related to the lower Brij surfactant concentration ($\leq 0.2\%$) than that used in this study (1%). When the washing and surfactant adsorption processes are interpreted together, it can be concluded that within the first 60 min of interaction, surfactant adsorption and solubilization with washing solution occurred to the same degree (Fig. 3). With time, adsorption of the surfactant on unpolluted soil continued, reflecting a continuous decrease in COD concentration. On the

other hand, the adsorption and release of organic constituents and fluorene from the contaminated soil seemed to occur concomitantly.

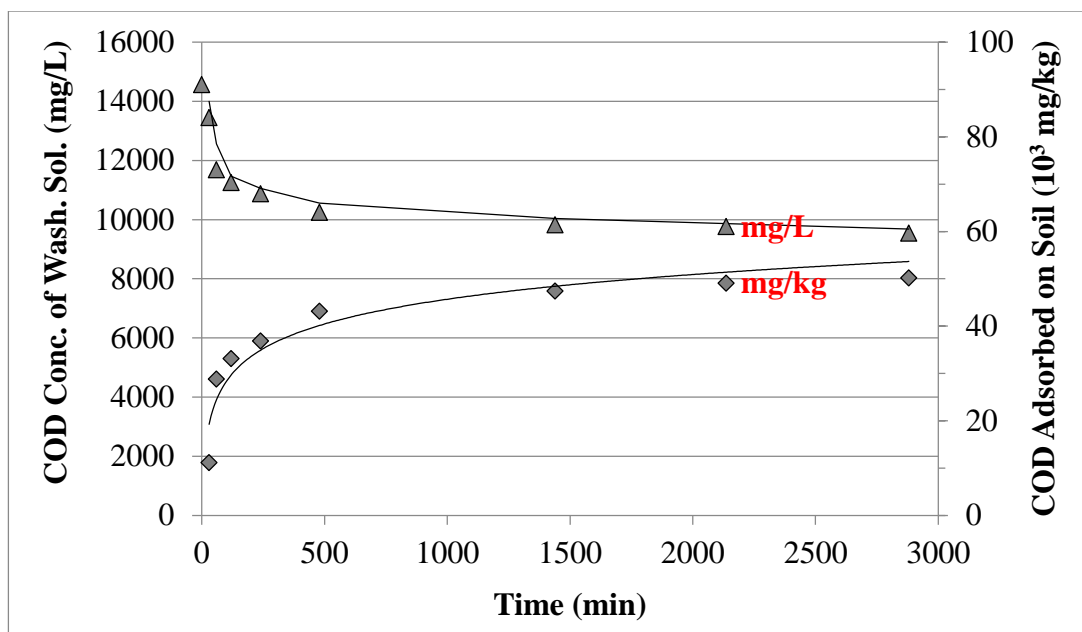


Figure 4. The influence of time on 1% Brij 58 adsorption presented as the COD concentration and amount of COD adsorbed on the soil (soil/solution: 1/10).

During this adsorption-desorption process of organic molecules, adsorption seemed to be the prevailing process, as the COD level in solution remained lower than the initial COD concentration (Fig. 3). The continuous release of fluorene from soil (Fig. 2) implied that other organic molecules in solution (Brij 58 and dissolved soil organic matter (DOM)) were involved in the adsorption-desorption process. In a study by Liang et al. [57] on the co-solubilization of phenanthrene and pyrene with the non-ionic surfactant Triton X-100 (TX 100), it was observed that polar SOM was dissolved during the washing process. It was stated that the combination of TX 100 with dissolved soil organic matter may have contributed to the higher phenanthrene desorption efficiency. Yu et al. [58] observed higher PAH release with the coexistence of a biosurfactant and DOM that was previously extracted from either food waste compost or soil. Similarly, Cheng and Wong [59] found enhanced desorption of PAHs from soil when DOM derived from pig manure compost was used together with Tween 80. Thus, it is believed that the high removal efficiencies observed for fluorene were a result of the combined influence of organic matter dissolved from the soil and the relatively low level of Brij adsorption. The hydrophobic nature of the surfactant, DOM and PAH compounds plays a crucial role at the soil-solution interface.

3.2.2. The influence of the Brij 58 concentration on fluorene solubilization

The effect of Brij 58 concentration on fluorene removal was investigated by carrying out identical experiments (soil-to-solution ratio of 1/10; reaction time of 24 h) using Brij 58 concentrations between 0.1% and 5%. As shown in Fig. 5, fluorene removal was negligible for a Brij concentration of 0.1%, which is well above the CMC of Brij 58 but below its effective CMC. The effective CMC, which is the CMC determined for a soil-water system, is higher than the CMC for a water system, meaning that higher surfactant doses are required for micelle formation [11]. The reason for this phenomenon is that surfactants at a dose below the effective CMC interact with the soil-water and soil-PAH interfaces as monomers and are rather consumed for adsorption. When the surfactant concentration is increased above the effective CMC, surfactants replace the water molecules and thus decrease the polarity of water and surface tension [60]. At higher concentrations, the saturation of the soil surface is enhanced, meaning that a stationary level in the surfactant-soil interaction is achieved and thus free-state surfactants are available for micelle formation [35,61]. With the help of hydrophobic tails, PAHs are encapsulated and thus partitioned into the core of micelles [62,63]. Such an elevated removal efficiency was observed when the Brij concentration increased to 1%. A further increase in Brij concentration continued to increase the fluorene removal, but at a lower rate, reaching removals of 285 mg/kg and 77.27% for a Brij 58 concentration of 5%. As the increase in fluorene removal efficiency from 60.34% to 77.24% was not found to be economically feasible, a Brij 58 concentration of 1% was accepted as the optimum concentration for use in further studies.

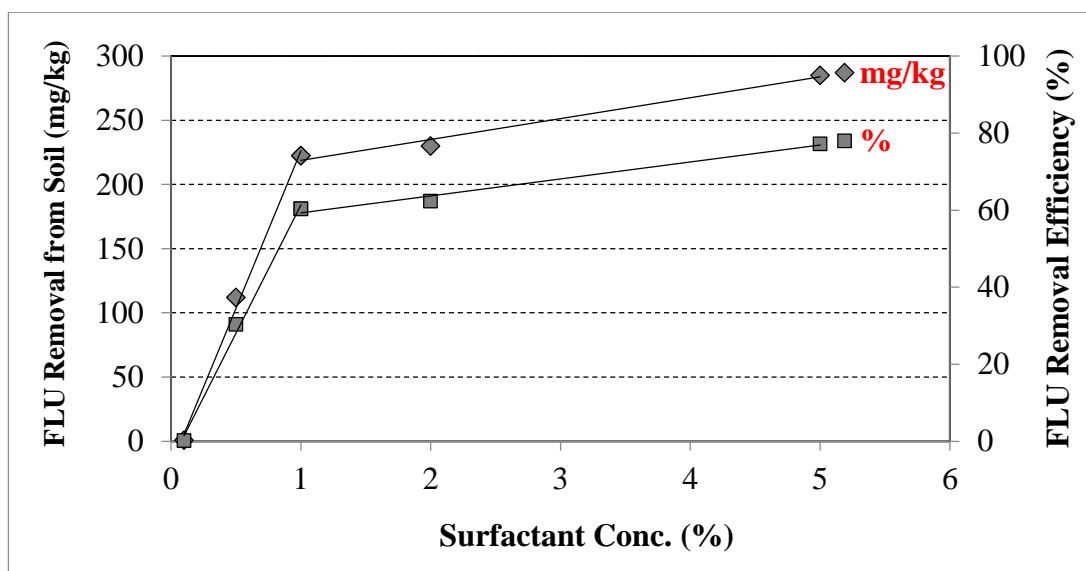


Figure 5. The influence of the percentage of Brij 58 in the washing solution on fluorene removal (soil/solution: 1/10).

Regarding the change in COD concentration with respect to Brij 58 concentration, similar trends were observed for the initial COD concentration and COD concentration after washing (Fig. 6). The initial COD concentrations increased from 2643 mg/L to 28750 mg/L, and the COD concentration after washing increased from 2150 mg/L to 25725 mg/L when the Brij concentration increased from

0.1% to 5%. The difference in concentrations again indicated surfactant adsorption, which seemed to increase with increasing Brij 58 concentration.

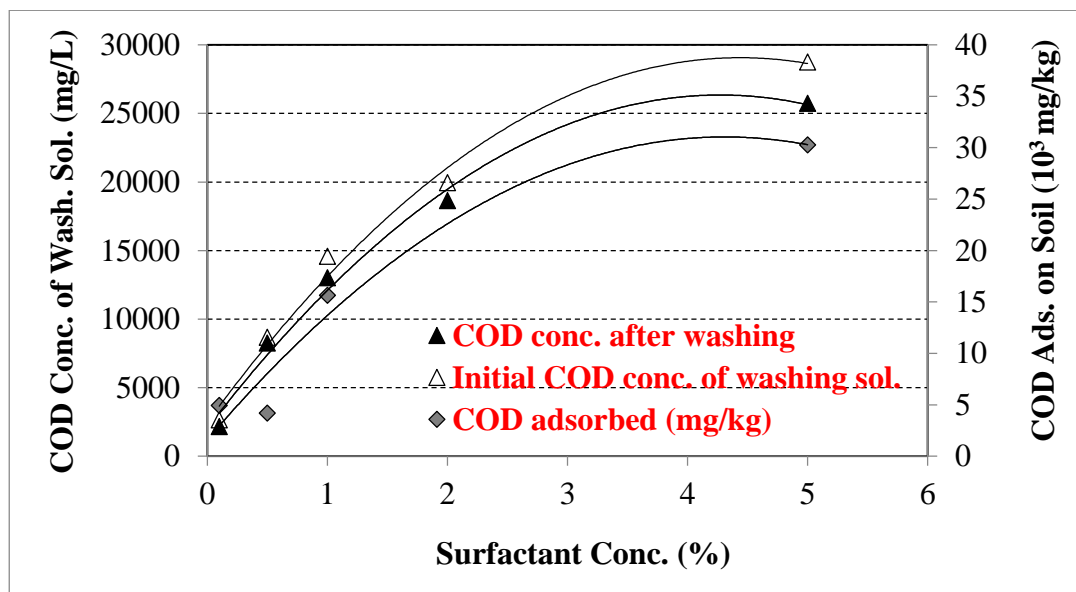


Figure 6. The influence of the percentage of Brij 58 on the COD concentration of the solution before and after washing and the amount of COD adsorbed onto the soil (soil/solution: 1/10).

3.2.3. The influence of the soil-to-solution ratio on fluorene solubilization

The influence of the soil solution ratio on fluorene removal was investigated by repeating the experiments with 1% and 5% Brij 58 concentrations under identical experimental conditions (reaction time 24 h) using soil-to-solution ratios varying between 1/2 and 1/20. Decreasing the soil-to-solution ratio resulted in an increase in fluorene removal efficiency. With 1% Brij 58, the fluorene removal efficiency increased from 9.09% to 64.13% by decreasing the soil-to-solution ratio from 1/2 to 1/20, corresponding to an increase of 33.52 mg/kg to 236.52 mg/kg fluorene removal, respectively. When 5% Brij 58 was used, an increase from 33.72% to 68.39 % and 124.36 mg/kg to 252.26 mg/kg were observed, respectively (Fig. 7). As lower soil-to-solution ratios cause higher consumption of washing solutions and thus more post-treatment of wastewater, a ratio of 1/5 seemed relatively feasible [11].

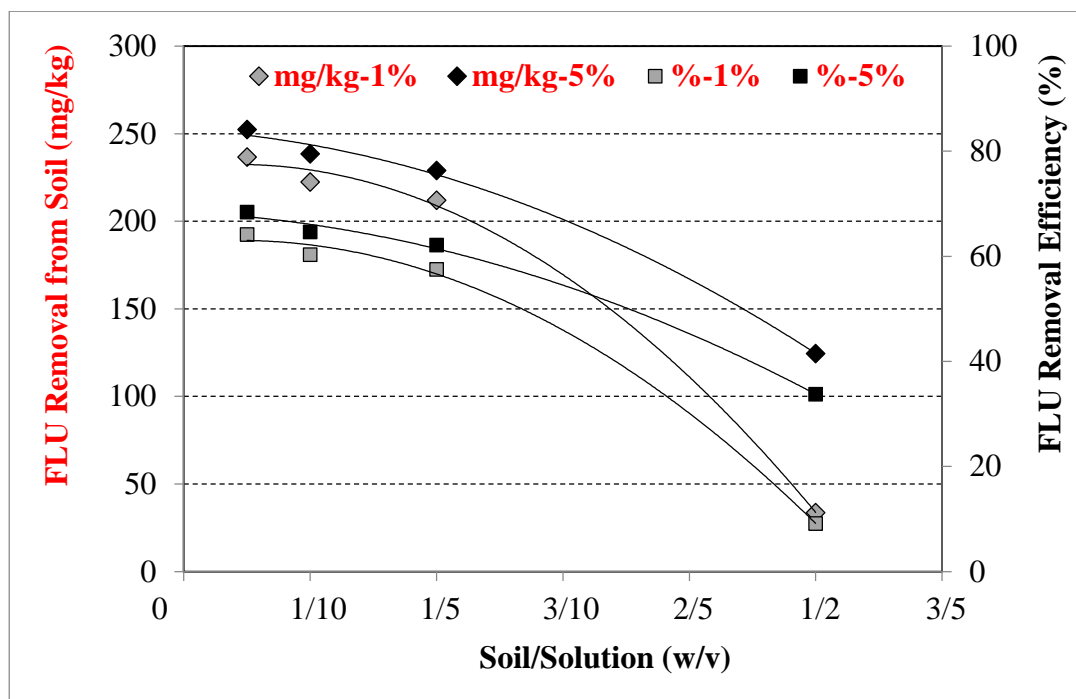


Figure 7. The influence of the soil-to-solution ratio on fluorene removal with 1% and 5% Brij 58 (reaction time: 24 h).

The changes in COD concentrations were quite interesting when the data of 1% and 5% Brij were interpreted together. For both Brij 58 concentrations, the COD concentrations of the washing solution reduced to lower values, decreasing with increasing soil-to-solution ratio (Fig. 8). However, the influence of the soil-to-solution ratio on the COD concentration of the 1% Brij 58 solution was not as important as that observed for the 5% Brij 58 solution. Accordingly, with a change in the soil-to-solution ratio from 1/20 to 1/2, the availability of Brij 58 in solution declined from 13625 mg/L to 11630 mg/L for 1% Brij and from 23000 mg/L to 14112 mg/L for 5% Brij. Regarding the ratio of available Brij to the adsorbed fluorene per gram of soil on a molar basis, it can be concluded that the data reflected a decreasing trend. Thus, for relatively higher soil-to-solution ratios, higher Brij 58 concentrations are required to reduce the surface tension and ensure sufficient availability of surfactant in solution [64].

Additionally, remembering that the initial COD concentrations of the 1% and 5% Brij solutions were 14562.5 mg/L and 28750 mg/L, respectively, the difference in concentrations again indicated to surfactant adsorption, which seemed to increase with decreasing soil-to-solution ratio. Thus, the amount of Brij 58 retained per gram of soil was lowest for a soil-to-solution ratio of 1/2, yielding 5.87×10^3 mg/kg and 29.28×10^3 mg/kg for 1% and 5% Brij 58 solutions, respectively. These values increased to 18.75×10^3 and 115×10^3 mg/kg for 1% and 5% Brij 58 solutions, respectively, when the soil-to-solution ratio decreased to 1/20. Huseyin and Ismail [64] reported a different trend and stated that the number of moles of surfactant adsorbed per gram of soil was constant and independent of the soil-to-solution ratio.

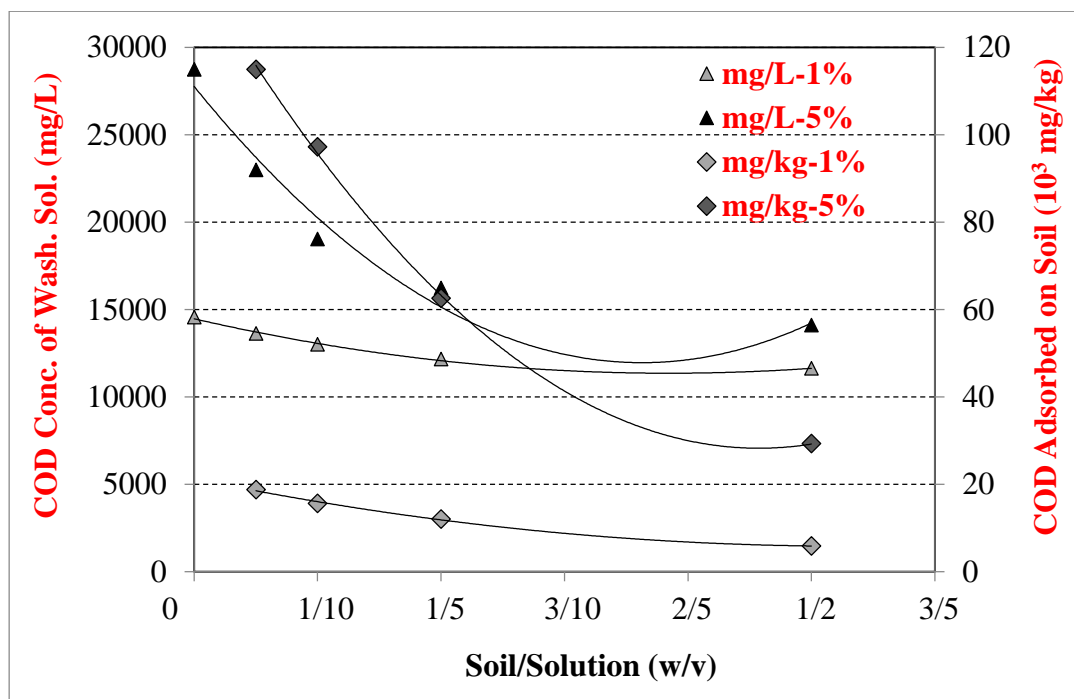


Figure 8. The influence of soil/solution on the COD concentration in washing solution and the amount of COD adsorbed on soil for 1% and 5% Brij 58.

3.3. Fluorene removal with the E-Fenton process

The E-Fenton process used in this study relied on the electro-generation of ferrous iron from the anode. Operational parameters such as reaction time, current density, and conductivity were investigated to determine the optimum conditions.

3.3.1. The influence of reaction time on PAH removal with the E-Fenton process

The effect of reaction time (15-120 min) on fluorene removal was studied using 2% H₂O₂, a current density of 15 mA/cm² and a conductivity of 6 mS/cm. The results in Fig. 9 show different trends for fluorene and COD removal. Fluorene removal reflected an initial fast removal of 82.76% within the first 15 min, continuing to increase with a decreasing rate and finally reaching an efficiency of approximately 92% in 120 min. The COD removal followed a continuous increasing trend, reaching efficiencies of 14.92% and 88.06% for 15 min and 120 min, respectively. This continuous increasing trend in COD removal may be attributed to the linear release of iron into the solution with time. The measured iron concentration was 388.89 mg/L, 755.56 mg/L, 1777.78 mg/L and 4933.33 mg/L at 15, 30, 60 and 120 min, respectively. These results imply that fluorene was preferentially removed from the washing solution within a very short time period (15 min). Additionally, oxidation conditions were capable of oxidizing Brij 58 and other organic compounds (e.g., humic compounds) in the washing solution. Regarding the energy consumption observed for a current density of 15 mA/cm², an increase from 7.04 kWh/m³ to 28.84 kWh/m³ was observed with an increase in reaction time from 15 min to

120 min. The calculated energy consumptions per amount (kg) of fluorene increased from 105.04 kWh/kg to 429.92 kWh/kg. A reaction time of 60 min was chosen to ensure high efficiencies for all experimental conditions and reduce energy consumption.

The E-Fenton process was evaluated using pseudo- first and –second order kinetic models. The first order rate constants for fluorene and COD were calculated as 1.6×10^{-2} 1/min and 1.8×10^{-2} 1/min, respectively, and the half lives ($t_{1/2}$) were 43 and 38 min, respectively. The correlation coefficient observed for fluorene ($r^2=0.59$) was lower than that observed for COD ($r^2=0.99$), but when the first-order kinetic data of fluorene was split into two kinetic stages, the correlation coefficients increased to $r^2_{\text{fast}}= 0.75$ and $r^2_{\text{slow}}= 0.86$. The corresponding reaction rates ($k_{\text{fast}}= 5.8 \times 10^{-2}$ 1/min and $k_{\text{slow}}= 0.8 \times 10^{-2}$ 1/min) also seemed to verify the two kinetic stages in fluorene removal. The correlation coefficients observed for the pseudo-second-order rate model were $r^2=0.86$ and $r^2=0.92$ for fluorene and COD removal, respectively. Thus, the pseudo-second-order rate model also described fluorene removal, but COD removal was better presented by the pseudo-first-order rate model. The second-order rate constants were determined to be 1.1×10^{-3} L/mg min and 3.7×10^{-6} L/mg min for fluorene and COD removal, and the half-lives ($t_{1/2}$) were 12 and 16 min, respectively. This kinetic evaluation implies that the oxidation of fluorene was faster than the oxidation of organic compounds in the Brij washing solution and therefore required lower reaction times to achieve efficiencies above 80%.

These results also implied that the micelle structure did not act as a barrier and inhibited the reaction of hydroxyl radicals with fluorene. Previous studies reported that the micelle structure act like a protection and therefore require destruction to enable the contact of radical with contaminant within the micelle, causing to higher oxidant doses [20,65]. Considering the difference between the fluorene and COD concentrations, removal trends and kinetic data, it can be concluded that the hydroxyl radicals reacted preferentially with fluorene. Trellu et al. [20] explained that organic contaminants with relatively smaller octanol-water partition coefficients (less hydrophobic) are posed closer towards the external shape of micelle rather than the center of micelle. Flotron et al. [66], on the other hand, stated that the interaction of Brij 35 and hydroxyl radicals was not rapid. Thus, the high efficiencies observed for fluorene seemed to be a result of both fluorene and Brij 58 characteristics.

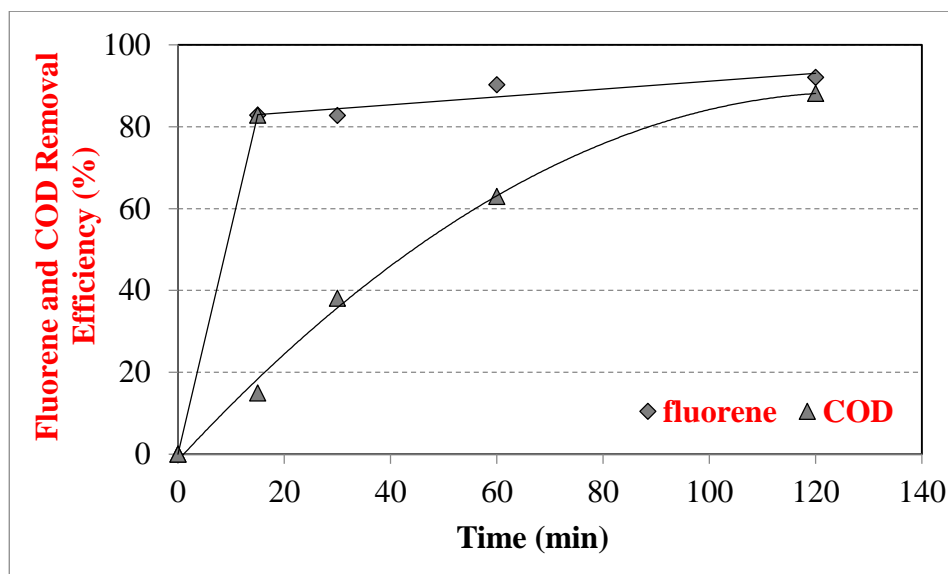


Figure 9. The influence of reaction time on fluorene and COD removal efficiencies with the E-Fenton process (current density: 15 mA/cm², %2 H₂O₂, EC: 6 mS/cm).

3.3.2. The influence of current density on PAH removal with the E-Fenton process

The effect of current density on fluorene removal was examined with current densities varying between 5 and 20 mA/cm². The experiments were repeated under identical conditions (2% H₂O₂ and 6 mS/cm) for the determined optimum time period. With the increase in current density, the potential difference between electrodes increased, which led to a higher release of ferrous iron (Fe(II)) from the electrodes. As more Fe(II) was available in the washing solution, the Fenton process was more catalyzed, resulting in higher oxidation efficiencies. As seen from Fig. 10, the oxidation of fluorene (76%) only nonsignificantly increased (< %3) with an increase in current density from 5 mA/cm² to 20 mA/cm². The COD removal efficiency continuously increased from approximately 37% to 84.25% when the current density was increased to 20 mA/cm². Thus, fluorene removal was not found to be dependent on current density levels above 5 mA/cm², meaning that the level of iron release did not influence fluorene removal, but the oxidation of dissolved organic compounds in the Brij 58 washing solution was strongly dependent on available Fe(II) ($r^2=0.999$). The Fenton reaction relies on the activation of hydrogen peroxide with a Fe(II) catalyst for hydroxyl radical generation [67]. Thus, when the availability of Fe(II) is limited, radical generation is insufficient for total contaminant oxidation. In the case of COD removal, the efficiency increased as more Fe(II) was generated with increasing current density. The ferrous iron concentrations measured were 262.89 mg/L, 1191.67 mg/L, 1987.66 mg/L and 3637.11 mg/L for 5, 10, 15 and 20 mA/cm², respectively, representing a linear trend. To ensure maximum fluorene removal, the optimum current density was chosen to be 15 mA/cm².

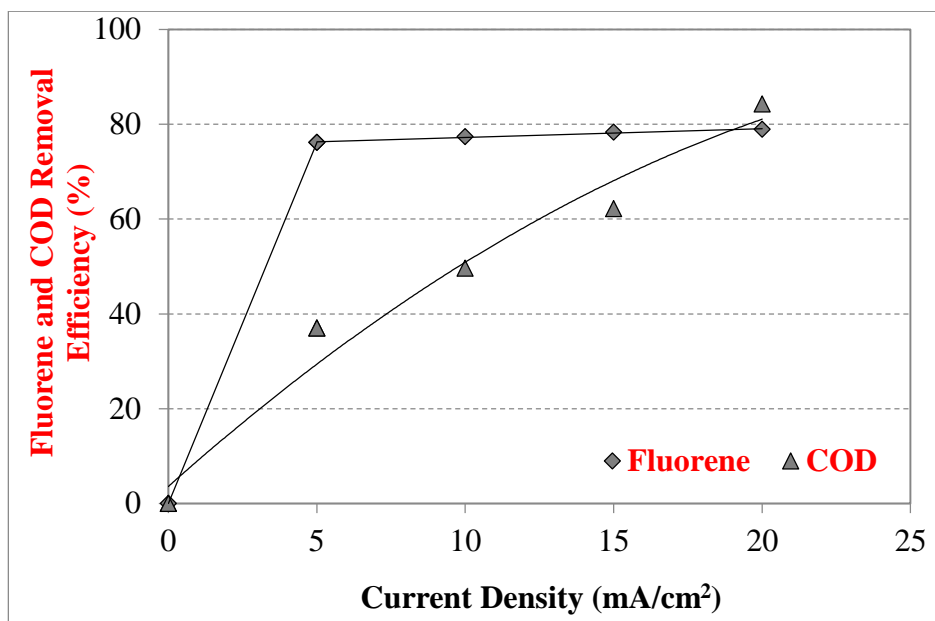


Figure 10. The influence of current density on fluorene and COD removal efficiencies with the E-Fenton process (2% H₂O₂, EC: 6 mS/cm, reaction time: 60 min).

3.3.3. The influence of electrical conductivity on PAH removal with the E-Fenton process

Electrical conductivity (EC) is an important process parameter affecting the electric current density in the washing solution. Thus, higher EC values were expected to increase the process efficiency. The effect of the EC of the washing solution on fluorene removal was investigated by applying different EC levels (2 - 18 mS/cm). As the EC value of the washing solution was very low, solid NaSO₄ was added into the washing solution before oxidation. Experiments were carried out with 2% H₂O₂ for a reaction time of 60 min and a current density of 15 mA/cm². Different trends in fluorene and COD removal efficiencies were observed (Fig. 11). As the EC of the washing solution increased from 2 mS/cm to 18 mS/cm, the fluorene removal efficiencies slightly increased from 92.8% to 98.8%. In contrast, the COD removal efficiency decreased from approximately 68% to 52%, respectively. This was attributed to a decrease in the voltage gradient between electrodes with the increase in EC of the washing solution. With an increase in EC from 2 mS/cm to 18 mS/cm, the voltage between electrodes decreased from 10.90 V to 4.30 V. As a result of the decrease in the voltage gradient between electrodes, anodic oxidation decreased, causing a reduction in the release of iron. The ferrous iron concentrations measured were 2366.67 mg/L, 1888.89 mg/L, 1633.33 mg/L and 1333.33 mg/L for 2, 6, 12 and 18 mS/cm, respectively. These results were in line with those of the studies of Orkun [68]. Additionally, reduced COD removal efficiencies support the reuse of the Brij 58 surfactant solution under specific conditions [69]. Due to the nonsignificant increase (approximately 6%) in fluorene removal, the optimum EC of washing solution was selected to be 2 mS/cm.

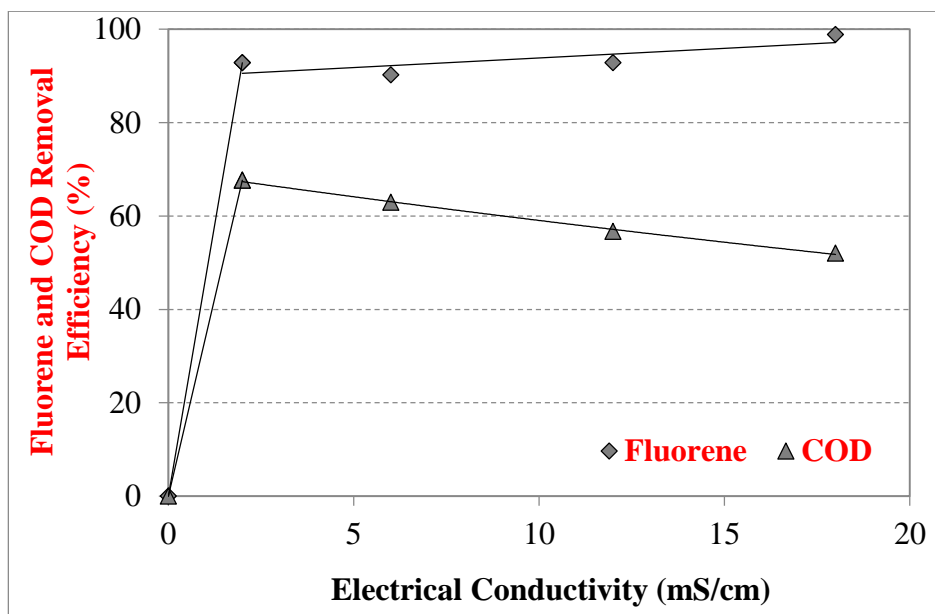


Figure 11. The influence of electrical conductivity on fluorene and COD removal efficiencies with the E-Fenton process (%2 H₂O₂, current density: 15 mA/cm², reaction time: 60 min).

4. CONCLUSIONS

The combined effects of soil washing and E-Fenton processes were investigated to achieve higher PAH removal efficiencies. The non-ionic surfactant Brij 58 was capable of solubilizing most of the adsorbed fluorene despite its attenuation by soil, which seemed to occur with two different sorption rates. Brij adsorption and release of organic constituents and fluorene from the contaminated soil seem to occur at the same time. Fluorene removal efficiencies increased with higher surfactant concentrations but decreased with increasing soil-to-solution ratios. Optimum operational parameters of the washing process were determined to be a 1440 min treatment time, a 1% Brij 58 concentration, and a 1/5 soil-to-solution ratio. Chemical oxidation experiments additionally indicated that Brij 58 did not inhibit the destruction of fluorene. The kinetic evaluation of E-Fenton oxidation reflected a faster destruction of fluorene when compared with the oxidation of Brij 58 and some other dissolved constituents (represented as COD). The influence of treatment time, current density, and electrical conductivity did not seem to have an important effect on fluorene removal but enhanced the oxidation of Brij 58, resulting in higher COD removal efficiencies. The continuous increasing trend observed for COD removal was related to the high availability of ferrous iron in solution, which was related to higher anodic release.

The combination of soil washing with E-Fenton oxidation will not only ensure high fluorene removal efficiencies but also give the opportunity to destroy fluorene and reserve Brij 58 when the operational parameters are assigned fit for purpose. Accordingly, relatively lower E-Fenton treatment times and current densities will allow both high fluorene removal efficiencies and the reuse of washing solution. Additionally, washing solutions require treatment before discharge; appropriate operational parameters can be determined to meet higher COD removal efficiencies necessary to meet the

discharge criteria. Thus, combined effects through selective oxidation of target compounds may serve as alternative treatment strategies for on-site applications.

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References

1. S. Gitipour, G.A. Sorial, S. Ghasemi and M. Bazyari, *Environ. Monit. Assess.*, 190 (2018) 546.
2. S. Zeng, J. Ma, Y. Ren, G.-J. Liu, Q. Zhang and F. Chen, *Int. J. Environ. Res. Public Health*, 16 (2019) 4928.
3. W.-J. Hong, Y.-F. Li, W.-L. Li, H. Jia, N.H. Minh, R.K. Sinha, H.-B. Moon, H. Nakata, K.H. Chi, K. Kannan and E. Sverko, *Sci. Total Environ.*, 711 (2020) 135223.
4. O. Idowu, K.T. Semple, K. Ramadass, W. O'Connor, P. Hansbro and P. Thavamani, *Environ. Int.*, 123 (2019) 543.
5. D. Lerda, Polycyclic Aromatic Hydrocarbons (PAHs) Factsheet, 4th edition, JRC Technical Notes, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, JRC 66955 (2011) Belgium.
6. K. Ciarkowska, F. Gambus, J. Antonkiewicz and T. Koliopoulos, *Chemosphere*, 229 (2019) 214.
7. M.M. Orazi, A.H. Arias, A.L. Oliva, A.C. Ronda and J.E. Marcovecchio, *Chemosphere*, 240 (2020), 124847.
8. W. Wilcke, *J. Plant Nutr. Soil Sci.*, 163 (2000) 229.
9. European Environment Agency (EEA), Contamination From Local Sources, (2009) <http://www.eea.europa.eu/themes/soil/soil-threats> (last accessed July 2020)
10. P. Haapea and T. Tuhkanen, *J. Hazard. Mater. B*, 136 (2006) 244.
11. A.A. Befkadu and Q. Chen, *Pedosphere*, 28 (2018) 383.
12. F. Lui, N. Oturan, H. Zhang and M.A. Oturan, *Chemosphere*, 249 (2020) 126176.
13. S. Kuppusamy, P. Thavamani, K. Venkateswarlu, Y.B. Lee, R. Naidu and M. Megharaj, *Chemosphere*, 168 (2017) 944.
14. A.T. Bessa, D. Bekele, R. Naidu and S. Chadalavada, *Environ. Technol. Inno.*, 9 (2018) 303.
15. H. Lu, W. Wang, F. Li and L. Zhu, *Sci. Tot. Environ.*, 653 (2019) 658.
16. Y. Li, X. Liao, S.G. Huling, T. Xue, Q. Liu, H. Cao and Q. Lin, *Sci. Tot. Environ.*, 647 (2019) 1106.
17. T. Zhang, Y. Lui, S. Zhong and L. Zhang, *Chemosphere*, 246 (2020) 125726.
18. P.V. Nidheesh and R. Gandhimathi, *Desalination*, 299 (2012) 1.
19. E. Mousset, E.D. Huguenot, E.D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito and M.A. Oturan, *Environ. Pollut.*, 211 (2016) 354.
20. C. Trelu, N. Oturan, Y. Pechaud, E.D. van Hullebusch, E.G. Esposito and M.A. Oturan, *Water Res.*, 118 (2017) 1.
21. C. Sandu, M. Popescu, E. Rosales, E. Bocos, M. Pazos, G. Lazar and M.A. Sanromán, *Chemosphere*, 156 (2016) 347.
22. American Society for Testing and Materials (ASTM), Designation: D 422-63, Standard Test Method for Particle-Size Analysis of Soils, Annual Book of ASTM Standards, ASTM International, (1999) West Conshohocken, USA.
23. American Society for Testing and Materials (ASTM), Designation: D 4972-95a, Standard Test Method for pH of Soils, Annual Book of ASTM Standards, ASTM International, (1995) West Conshohocken, USA.
24. Soil Survey Staff, Soil Survey Manual, USDA. Handbook No: 18, (1993) Washington D.C.
25. Turkish Standards Institute (TSE), TS 8336 Determination of Soil Organic Matter, Ankara, (1990)

- (in Turkish).
26. H.H. Rump and H. Krist, Laboratory Manual for the Examination of Water Waste Water and Soil, 2nd Ed., ISBN 1560812214, (1992) Verlag Chemie, Weinheim, Germany.
 27. U.S. Environmental Protection Agency (EPA), A Resource for MGP Site Characterization and Remediation, EPA/542- R-00-005, Washington D.C., 2000.
 28. J. Gómez, M.T. Alcántara, M. Pazos and M.Á. Sanromán, *Chem. Eng. J.*, 2010 (159) 53.
 29. M. Kobya, E. Demirbaş, O.T. Can and M. Bayramoğlu, *J. Hazard. Mater.*, 132 (2006) 183.
 30. U.S. Environmental Protection Agency (EPA), Soxhlet Extraction, U.S. EPA Method 3540C, Washington, DC, 1986.
 31. T. Oluseyi, K. Olayinka, B. Alo and R.M. Smith, *Afr. J. Environ. Sci. Technol.* 5 (2011) 482.
 32. J.L. Santos, I. Aparicio and E. Alonso, *Anal. Chim. Acta*, 605 (2007) 102.
 33. American Public Health Association (APHA), Standard Methods for Examination of Water and Wastewater, 20th ed., APHA-AWWA-WPCF, (1998) 9 Washington, DC, USA.
 34. M. Amir, S. Mohsen and M. Afsaneh, *Soil Sediment Contam.*, 27 (2018) 200.
 35. F. Gharibzadeh, R.R. Kalantary, A. Esrafil, M. Ravanipour and A. Azari, *J. Environ. Health Sci. Eng.*, 17 (2019) 171.
 36. F.A. Bezza and E.M. Nkhambayausi-Chirwa, *Biotech. Biotechnol. Equip.*, 29 (2015) 680.
 37. C. Barnier, S. Ouvrard, C. Robin and J.L. Morel, *Sci. Total Environ.*, 470-471 (2014) 639.
 38. M. Wehrer, J. Mai, S. Attinger and K.U. Totsche, *Environ. Pollut.*, 179 (2013) 301.
 39. J.K. Saxe, H.E. Allen and G.R. Nicol, *Environ. Eng. Sci.*, 17 (2000) 233.
 40. M. Cheng, G. Zeng, D. Huang, C. Yang, C. Lai, C. Zhang and Y. Lui, *Chem. Eng. J.*, 314 (2017) 98.
 41. S. Lamichhane, K.C.B. Krishna and R. Sarukkalgige, *J. Environ. Manage.*, 199 (2017) 46.
 42. G. Cornelissen, P.C. Van Noort and H.A. Govers, *Environ. Sci. Technol.*, 32 (1998) 3124.
 43. B.I. Olu-Owolabi, P.N. Diagboya and K.O. Adebowale, *Geoderma*, 239-240 (2015) 179.
 44. M. Saeedi, Y.L. Loretta and J.R. Grace, *Environ. Earth Sci.*, 77 (2018) 305.
 45. J. Hu and M.D. Aitken, *Chemosphere*, 89 (2012) 542.
 46. G.C. Wang, Y. Zhou, X. Wang, X. Chai, L. Huang and N. Deng, *J. Hazard. Mater.*, 184 (2010) 690.
 47. L. Yang, M. Jin, C. Tong and S. Xie, *J. Hazard. Mater.*, 244-245 (2013) 77.
 48. A. Ukalska-Jaruga, B. Smreczak and A. Klimkowicz-Pawlas, *J. Soils Sediments*, 19 (2019) 1890.
 49. B.E. Özkaraova Güngör and M. Bekbölet, *Geoderma*, 159 (2010) 131.
 50. W. Zhou and L. Zhu, *Environ. Pollut.*, 147 (2007) 66.
 51. C.K. Ahn, Y.M. Kim, S.H. Woo and J.M. Park, *J. Hazard. Mater.*, 154 (2008) 153.
 52. M. Ishiguro and L.K. Koopal, *Adv. Colloid Interface Sci.*, 231 (2016) 59.
 53. P. Somasundaran, E.D. Snell and Q. Xu, *J. Colloid Interf. Sci.*, 144 (1991) 165.
 54. X. Liang, C. Guo, C. Liao, S. Liu, L.Y. Wick, D. Peng, X. Yi., G. Lu, H. Yin, Z. Lin and Z. Dang, *Environ. Pollut.*, 225 (2017) 129.
 55. B.J. Brownawell, H. Chen, W. Zhang and J.C. Westall, *Environ. Sci. Tech.*, 31 (1997) 1735.
 56. X.-H. Ma, L. Zhao, Z.-R. Lin and Y.-H. Dong, *Environ. Sci. Pollut. Res.*, 23 (2016) 7890.
 57. X. Liang, C. Guo, Y. Wei, W. Lin, X. Yi, G. Lu and Z. Dang, *Chemosphere*, 144 (2016) 583.
 58. H. Yu, *J. Hazard. Mater.*, 190 (2011) 883.
 59. K.Y. Cheng and J.W.C. Wong, *Chemosphere*, 62 (2006) 1907.
 60. M. Saeedi, Y.L. Loretta and J.R. Grace, *Pollution*, 6 (2020) 1.
 61. Z.Y. Chong, X.-Y. Liao, X.-L. Yan, L. Sun, D. Zhao and T. Liang, *Pedosphere*, 24 (2014) 209.
 62. Y. Gong, X. Zhao, R.E. O'Reilly, T. Qian and D. Zhao, *Environ. Pollut.*, 185 (2014) 240.
 63. W. Wei, Z. Ran, H. He, K. Zhou and Z. Huangfu, *Chemosphere*, 254 (2020) 126854.
 64. T.A. Huseyin and Z.Z. Ismail, *Environ. Technol.*, 34 (2013) 351.
 65. E. Mousset, N. Oturan, E.D. van Hullebusch, G. Guibaud, G. Esposito and M.A. Oturan, *Water Res.*, 314 (2017) 98.
 66. V. Flotron, C. Delteil, A. Bermond and V. Camel, *Polycycl. Aromat. Comp.*, 23 (2003) 353.

67. H. He and Z. Zhou, *Crit. Rev. Env. Sci. Tec.*, 47 (2017) 2100.
68. M.O. Orkun, Investigation of the Treatment of Solid Waste Leachate by Electrochemical Methods, Ondokuz Mayıs University, Gradual School of Science, Environmental Engineering Department, Master of Science Thesis, Samsun, 2007, 222429 (in Turkish).
69. J.M. Rosas, F. Vicente, A. Santos and A. Romero, *Chem. Eng. J.*, 220 (2013) 125.

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