

Submerged Arc Breakdown of Sulfadimethoxine (SDM) in Aqueous Solutions

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Abstract Low voltage, low energy submerged pulsed arcs were used to break-down Sulfadimethoxine (SDM) contamination in aqueous solutions. The SDM concentration decreased exponentially with rate constants of $0.13\text{--}1.9\text{ min}^{-1}$ during processing by pulsed arcs with a pulse repetition rate of 100 Hz, energies of 2.6–192 mJ and durations of 20, 50 and 100 μs . The electrical energy consumption was minimized with short duration pulses— 1.5 kW-hr/m^3 with 7.5 mJ, 20 μs pulses for 90% SDM removal.

Keywords Submerged pulsed arc · Electro-hydraulic discharge · Water treatment · Antibiotic · Plasma

Introduction

Antibiotics, a subset product of the pharmaceutical industry, are among those emerging micro-contaminants of concern due to their extensive use in human therapy and veterinary medicine, and their potential adverse effects on the ecosystem and on human health [1–3]. Antibiotics are not entirely processed by our bodies, as more than 90% of the antibiotics used are secreted through urine and feces and may be detected in wastewater where the common treatment technologies are ineffective in their removal [4, 5]. There is growing concern about the potential impact of antibiotic residues on the environment as the majority of antibiotics administered are excreted unchanged, and given that land

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application of animal waste as a supplement to fertilizer is common practice [6]. These low-level contaminations of water supplies by antibiotic compounds may encourage the development of bacterial strains resistant to that antibiotic compound [7–9].

Several studies have detected pharmaceutical residues in surface and groundwater, probably from sewage and agricultural sources [10]. Pharmaceuticals have been identified in feeding waters for waterworks (rivers, bank filtrates and groundwater), as well as in many municipal sewage treatment plant effluents [11–13]. These studies reflect the need to implement a technological solution for removal of pharmaceutical residues and antibiotics in water and effluents to produce safe water for human consumption.

Sulfonamides, a group of synthetic antibiotics, are commonly used in food-producing animals as growth promoters and as therapeutic and prophylactic drugs for a variety of bacterial and protozoan infections [14]. Specifically sulfadimethoxine (SDM), a sulfonamide antibiotic, is known for its broad activity against multiple bacterial infections and in many animal species with coccidial infections. As such, the low cost of SDM and the wide use on regular basis in the livestock industry can potentially contribute to the environmental load. For example, traces of SDM in the U.S. streams probably reflect inputs from sewage and agricultural sources [10]. SDM concentrations were detected at concentrations ranging from 0.046 to 0.068 $\mu\text{g/l}$ in the local groundwater of Idaho, USA, from animal waste [15].

Several treatment technologies were suggested to breakdown SDM in water. The degradation of SDM was studied under a polychromatic UV lamp, and the results indicated that direct photolysis is not satisfactory as a fluence of about 5000 mJ/cm^2 is needed to break down 99% of SDM at pH 6.5 [16]. However others found that oxidation and chlorination was very efficient in removing SDM at typical doses in water treatment plant (WTP) [17]. Other studies showed that oxidation with free chlorine and monochloramine [18], ferrate (VI) [6] and ozonation [19] have great potential in removal of sulfonamides including SDM. To meet the challenges presented by continuously emerging trace contaminants and microbial contaminants, increasingly stringent regulations and rising of energy costs, new drinking water treatment technologies must be developed.

The pulsed submerged arc, sometimes referred to as an electro-hydraulic discharge, is a high-current electrical discharge between two electrodes in a liquid. A plasma bubble that consists of vaporized and partially ionized material from the liquid and the electrodes conducts the electrical current. It has been shown that plasma technologies have the capability to treat water using several mechanisms such as: radical reactions, shock waves, ultra-violet radiation, ionic reactions, electron processes and thermal dissociation [20–23]. It is suspected that these factors, singularly or synergistically, may be responsible for concurrently oxidizing trace contaminants and disinfecting microorganisms in water. The electro-hydraulic discharge has been shown to oxidize many organic compounds such as methyl-tert-butyl ether (MTBE), [24]; atrazine [25], phenol [26] and chlorobenzene [27] using high voltage electrical discharges.

Although electro-hydraulic discharge systems have been studied for many years, its use in water treatment applications is rather recent [28] and remains to be optimized for use in various types of contaminants and microorganisms. Specifically, neither the effectiveness of low voltage submerged arcs in micro-contaminant removal, nor submerged discharges in general in SDM removal, have been reported previously. The objective of this research was to determine the effectiveness of low voltage, low energy submerged pulsed arc treatment in breaking down an antibiotic compound in aqueous solutions. The specific goals of this study were to (1) study the degradation kinetics of SDM at various pulse energies and durations, and (2) model SDM removal in an aqueous solution.

Experimental Details

Arc Treatment Apparatus

Pulsed arcs were applied between two 99.5% carbon electrodes submerged in spiked water as illustrated in Fig. 1. An L-shaped stationary electrode has a 4 cm² plate work piece. A second electrode, a 4 mm diameter rod with a 28° conical tip, was mounted on a vibrator, so as to periodically contact and separate from the first electrode plate, at a vibration frequency of 100 Hz, vibration amplitude of ~0.5 mm, for processing times up to 5 min. The arcs were ignited by applying a voltage between the electrodes from a charged capacitor. A current pulse and plasma are produced during each contact event. The energy stored in the capacitor $W = \frac{1}{2}CU_c^2$ (where C and U_c are the capacitance and capacitor charge voltage, respectively) and the pulse duration τ were varied by varying C and U_c .

Pulses with a duration of 20 μ s and energies of 2.6, 7.5, and 16 mJ stored in a C = 5 μ F capacitor were used. In some experiments, longer pulses, of 50 and 100 μ s, with energies of 7.7, 22.7 and 48 and 30.7, 90.7, and 192 mJ stored in C = 15 μ F and 60 μ F capacitors, respectively, were also used. A 100 MHz, two-channel oscilloscope connected to a PC was used for measuring and recording arc voltage and current waveforms.

Chemicals

SDM standard (99.9% purity) was obtained from Sigma-Aldrich, ULC grade methanol, acetonitrile and water from Bio-Lab Ltd. (Jerusalem, Israel). The molecular structure of SDM is presented in Fig. 2. SDM stock solution was prepared by dissolving the compound in methanol at a concentration of 100 mg/l. All chemicals were used as obtained and working solutions were prepared with ULC grade water. A 20 ml sample was spiked with SDM at an initial concentration of 1 μ g/ml and subjected to the submerged arc treatment. Samples were collected over a minimum of four targeted processing times between 0 and 5 min.

Fig. 1 Apparatus of electrical discharge

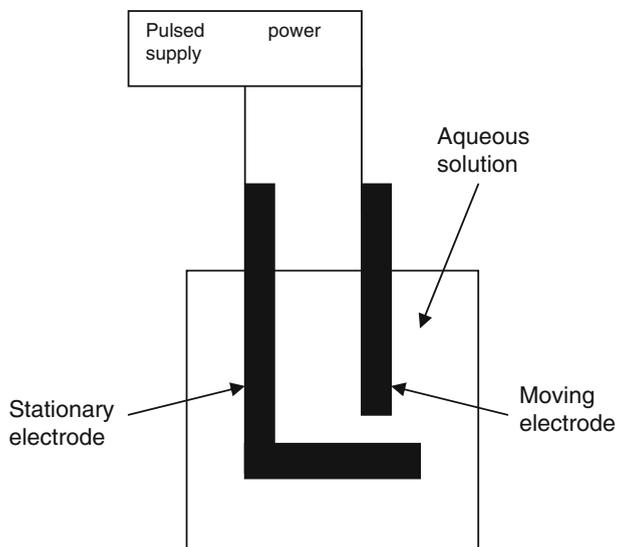
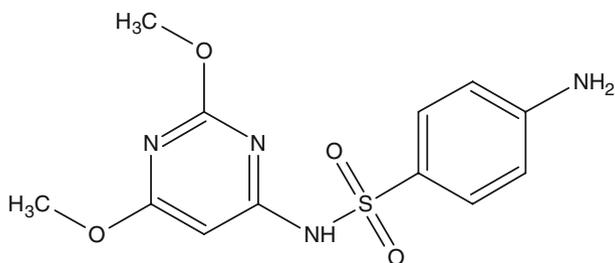


Fig. 2 The molecular structure of Sulfadimethoxine (SDM)—
The model pollutants



Detection and Characterization of Antibiotic residues

The solution subjected to the submerged arc treatment was immediately filtered by 0.22 μm PTFE disk filter (47 mm diameter) using a vacuum pump. A sample containing 1 ml of the filtered solution was injected into a vial. The vials were analyzed by a High Performance Liquid Chromatography (HPLC) system (Agilent 1100 series) equipped with a diode UV detector (DAD). Absorption was monitored in the wavelength range of 260–280 nm. The selected liquid chromatography (LC) column was a silica-based C18 (ACE, 2.1 mm \times 250 mm). The mobile phase consisted of a multi-step gradient combining (A) 0.1% formic acid (FA) in water (pH 3.4), and (B) 0.1% FA in Acetonitrile. In order to obtain high resolution separation of SDM (peak width <0.8), a gradient was used at a flow rate of 0.5 ml min^{-1} .

In order to increase the detection sensitivity, a Mass Spectrometer (MS/MS) system (Finnigan LCQ) was used in the positive electro-spray ionization (ESI) mode. The flow exiting the HPLC was passed through a split connector with 60 l/min introduced into the MS interface. Ions in the range 85–400 m/z were registered in the conventional scanning mode. Instrument control, data acquisition and evaluation were performed with Xcalibur software (Table 1).

The MS/MS ‘Selected Reaction Monitoring’ (SRM) feature was used. This provided good selectivity, specificity, and sometimes a lower detection limit than full scan MS. The conditions for the measurement of precursor ions were optimized in the single MS scan mode. Exclusively protonated or deprotonated molecular ions were used as precursors for the MS/MS experiments. Details of the measurement conditions of SDM, precursor and product ions are shown in Table 2.

Table 1 HPLC gradient for the separation of SDM

| Time (min) | % Solvent A | % Solvent B |
|------------|-------------|-------------|
| 0 | 65 | 35 |
| 2 | 15 | 85 |
| 5 | 15 | 85 |
| 7 | 65 | 35 |

Table 2 MS/MS conditions

| Antibiotic | Retention time (min) | Precursor ion $[M + H]^+$ | Collision energy [V] | Product ion 1 (MS/MS) |
|------------|----------------------|---------------------------|----------------------|-----------------------|
| SDM | 3.57 | 311 | 17 | 156, 218, 245 |

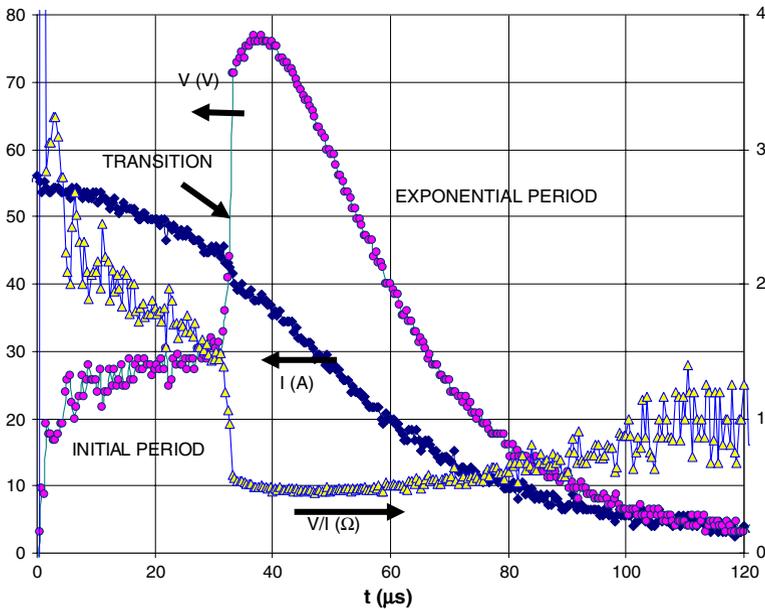


Fig. 3 Typical current and voltage pulse waveforms for $W = 91$ mJ and $C = 60$ μF

Results and Discussion

Discharge current and voltage waveforms varied somewhat from pulse to pulse—a typical example for a discharge with stored energy $W = 91$ mJ and capacitance $C = 60$ μF is presented in Fig. 3. At first, a current of ~ 25 – 30 A flowed for a period of ~ 30 μs , and then there was a sudden transition in which the current increased to ~ 76 A, followed by an exponential decrease in the current with a time constant of ~ 24 μs . During all of this time the potential between the electrodes decreased from its initial value of ~ 55 V. Also plotted in Fig. 3 is the instantaneous ratio of the voltage and current, V/I . It is seen that during the initial period, V/I decreased with time from about 2.5 to 1.5 Ω , while during the exponential period, V/I was at first a relatively constant 0.5 Ω , and then rose towards the tail of the current pulse to ~ 1 Ω . Bright light is emitted from the vicinity of the gap between the electrodes during the discharge. During treatment, the solution temperature increased slightly, e.g. from 19.5°C to 24.0°C after 5 min arc treatment by pulses generated with $C = 60$ μF and $W = 192$ mJ.

Plasma generation may be inferred from the bright light emitted during the discharge. Based on analysis of the waveform, and with the background of similar phenomena described in the switchgear literature, we tentatively infer that the following sequence of events occurred with each contact of the electrodes. The moving electrode approaches the stationary electrode at a velocity of 0.1 m/s. When the electrodes are sufficiently close, e.g. $\sim d = 3$ μm , which would occur about 30 μs before contact, a strong electric field is generated between the electrodes, i.e. $E = V/d \approx 19$ V/ μm , and the gap breaks down, starting the “initial period”. It is likely that the current jump (and corresponding step decrease in V of ~ 4 V) occurring at the transition point (at 30 s in Fig. 3) is caused by the contact of the two electrodes. No phenomenon is observed which clearly designates

separation, and thus possibly the contact is only instantaneous. The moving electrode would tend to bounce off of the stationary electrode. Upon separation, a “drawn arc”, well known in contact systems [29], is probably ignited: As the electrode break contact with each other, current is conducted by a single microscopic asperity which at the end remains in contact last. The current through this asperity super-heats and explodes it, and forms a metallic vapor plasma, which provides a conducting path between the separating electrodes. Shortly after transition, the current decreases exponentially, and the discharge resistance of $\sim 0.47 \Omega$ is the primary impedance in the discharge circuit. The exponential time constant was $\sim 24 \mu\text{s}$; during a period of 1 time constant the electrodes separate by approximately $2.4 \mu\text{m}$.

Breakdown of the antibiotic SDM was studied for a wide range of processing times and pulse energies and durations. Figure 4 illustrates an example of an HPLC chromatogram, obtained after processing the SDM solution by the submerged pulsed arc treatment at specific conditions. It is seen that the peak area decreases, and hence the antibiotic concentration decreases, with processing time. Measurements of pH of processed $1 \mu\text{g/ml}$ SDM solution in deionized water shown that it weakly depended on used pulse parameters (energy and duration), and varied in the range of 5.7–6.5.

Figure 5 demonstrates the degradation of $1 \mu\text{g/ml}$ of SDM in deionized water for various pulse parameters (energy and duration). The impact of the submerged pulsed arc treatment on the degradation of SDM was plotted by the natural logarithm of (C_0/C_t) as a function of processing time t , where C_0 and C_t are the initial antibiotic concentration and the concentration after processing time t . Regression analysis was used to fit the curve to the following equation:

$$\ln(C_0/C_t) = k t \quad (1)$$

where k is the pseudo-first-order decay rate constant (min^{-1}).

In all cases presented in Fig. 5, the reaction kinetics between $\ln(C_0/C_t)$ and t are linear. The data fitted using a linear regression approach resulted in pseudo-first order reaction kinetics which reflects the difference in degradation between samples. The slope of the lines in Fig. 5 provide the decay rate constant k as summarized in Table 3 as a function of pulse energy and pulse duration.

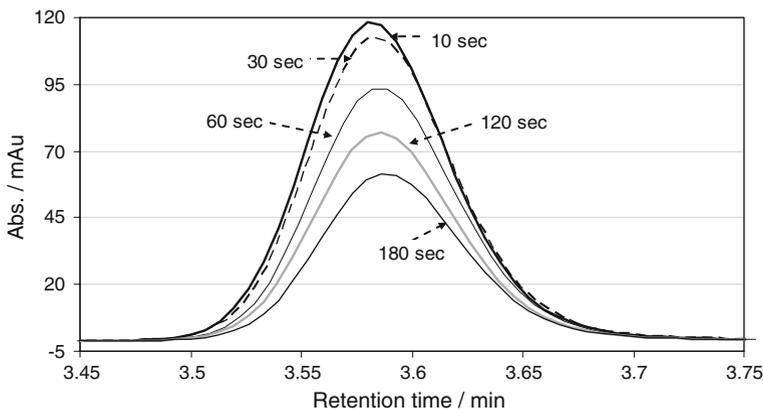


Fig. 4 Typical HPLC chromatograms of solutions containing SDM at a concentration of $1 \mu\text{g/ml}$ processed by a 48 mJ, $50 \mu\text{s}$ submerged pulsed arc

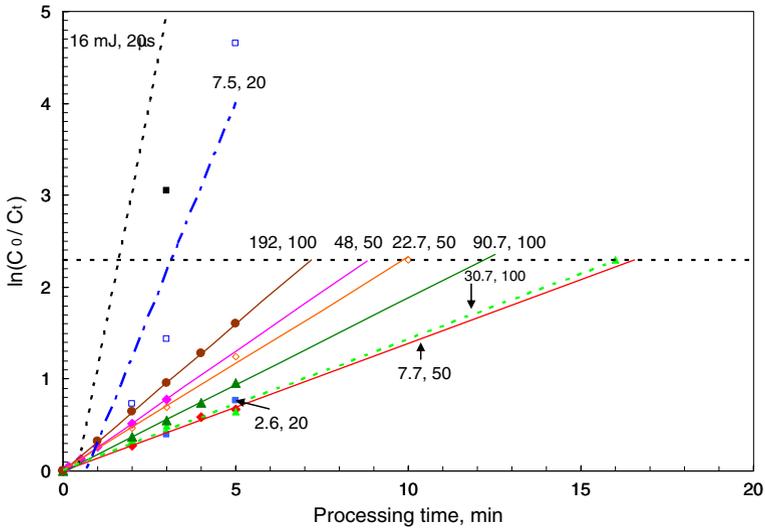


Fig. 5 Degradation of the antibiotic (SDM) versus processing time t for different energies stored by capacitor (W), and pulse durations (τ)

Table 3 Pseudo-first-order rate constant k and energy density E extrapolated for 90% and 99% SDM removal (according to Fig.5)

| Energy stored by capacitor (W) mJ | Pulse duration (τ) μ s | (k) min^{-1} | R -squared value | (E) kW-hr/m^3 90% | (E) kW-hr/m^3 99% |
|---------------------------------------|-----------------------------------|---------------------------|--------------------|--------------------------------|--------------------------------|
| 2.6 | 20 | 0.15 | 0.99 | 3.32 | 6.63 |
| 7.5 | 20 | 0.90 | 0.86 | 1.56 | 3.11 |
| 16 | 20 | 1.90 | 0.85 | 1.60 | 3.17 |
| 7.7 | 50 | 0.14 | 0.99 | 10.63 | 22.62 |
| 22.7 | 50 | 0.30 | 0.97 | 14.50 | 28.92 |
| 48 | 50 | 0.26 | 0.99 | 35.24 | 70.28 |
| 30.7 | 100 | 0.13 | 0.97 | 45.26 | 92.80 |
| 90.7 | 100 | 0.18 | 0.99 | 93.70 | 186.82 |
| 192 | 100 | 0.32 | 0.99 | 113.80 | 226.93 |

Note: Energy density data for 90% and 99% removal were extrapolated from the k value as data points did not reach such high removal at processing time experimented

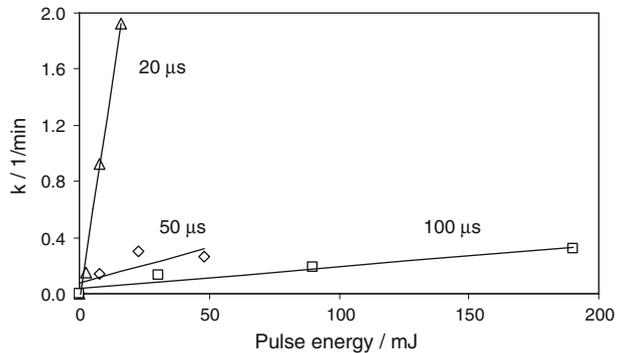
The energy density E (kW-hr/m^3) required for 90% and 99% SDM removal as a function of the energy W stored by the capacitor and τ pulse duration was extrapolated from the results as:

$$E = f \cdot t \cdot \frac{W}{V_t} \tag{2}$$

where f is the pulse frequency and V_t is the total volume (20 ml) of treated liquid.

The energy density E represents the electrical energy in kilowatt-hours per cubic meter (kW-hr/m^3) required for reduction of one order of magnitude (90% removal) or two orders (99%), assuming first order degradation kinetics in water contaminated with SDM. This

Fig. 6 Pseudo-first-order rate constant for decay of SDM as a function of pulse energy (W) for different pulse duration (τ)



term represents the electrical cost of the system and lower E values correspond to higher energy efficiencies. In Table 3 the more efficient processes were mostly obtained with the shorter pulse duration. Nevertheless, we have to note that a linear regression approach of shortest pulses was with lowest R -squared values. Reasons of the discrepancy will be further studied.

The pseudo-first-order rate constant k is shown as a function of the pulse energy W , with the pulse duration as a parameter, in Figure 6. It may be seen that for a given pulse duration, k increases linearly with W , and R -squared value were 0.99, 0.7, and 0.93 for pulse durations 20, 50, and 100 μ s respectively.

Angeloni et al. [24] found an optimum between energy input and Methyl tert-butyl ether (MTBE) removal in water by the pulsed arc electro hydraulic discharge (PAED) and suggested that regulatory discharge limits must be considered in order to achieve an appropriate cost-benefit compromise for removal of MTBE. PAED demonstrated to treat MTBE effectively; with over 99% removal achieved when the cumulative input energy exceeded 12 kW-hr/m³, and both detention time and arc electrode gap (i.e., discharge frequency) had a significant effect on the MTBE removal efficiency. In the current study, 99% removal of SDM in water was extrapolated from k values and resulted in energies between approximately 3.11–227 kW-hr/m³, with strong dependence of the efficiency on pulse duration. Further studies will investigate also impact of other parameters such as shorter pulse durations and electrode gap on SDM degradation at various water types.

Angeloni et al. [24] and others use high voltage (~ 10 kV) to initiate the discharge, and the arcs generally used very high currents, e.g. kA's. The low voltage technique used in the present study is easier and less expensive to implement than high voltage pulses, and thus may have the potential for encouraging industrial implementation.

Figure 7 illustrates the pseudo-first-order rate constant k as a function of the pulse duration (τ), with the pulse energy (W) as a parameter. It may be seen that for a given pulse energy, k decreased with pulse duration. The decrease is rapid for pulse duration between 25 and 50 μ s and slow for pulse duration between 50 and 100 μ s. This suggests that even shorter pulses should be investigated in the future.

A mathematical model was postulated to describe SDM removal, based on an assumption that during each pulse, a given antibiotic molecule was randomly located within a spherical region having volume V_k surrounding the discharge in which there is unity inactivation probability and that outside this region the inactivation probability is negligible. Thus if the total number of antibiotic molecules $N(0)$, comprising N_c complete and N_b broken-down molecules is constant, then

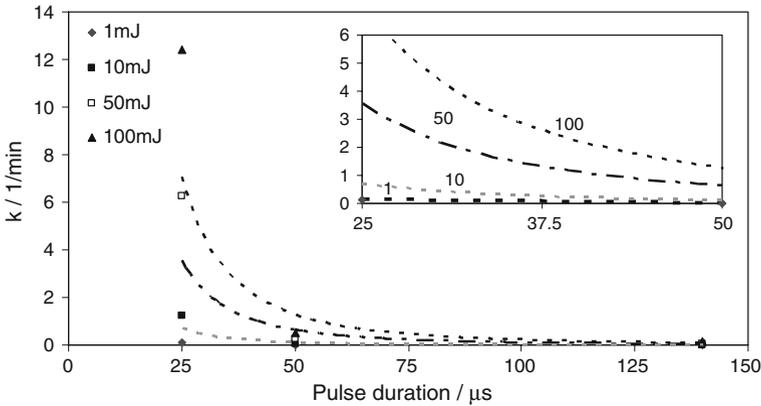


Fig. 7 Pseudo-first-order rate constant for SDM versus pulse duration (τ) for different energies stored in the capacitor W

$$\begin{aligned}
 N(0) &= N_c(t) + N_b(t) = N_c(0) \\
 \frac{dN_c(t)}{dt} &= -\frac{dN_b(t)}{dt} = -f \frac{N_c}{V_t} V_k = -kN_c \\
 \ln[N_c(0)/N(t)] &= \ln[C_0/C_t] = kt, \quad k = \frac{fV_k}{V_t}
 \end{aligned}
 \tag{3}$$

where k is the pseudo-first-order decay rate constant. The obtained natural logarithmic dependence agrees with Fig. 5. For example, let us consider processing by 48 mJ, 20 μ s pulses. From Fig. 5, 90% removal was obtained with 8.8 min of processing time ($C_0/C_t = 10$). Then, the rate constant is $k = 0.2614 \text{ min}^{-1}$, and the relative removal volume and removal radius may be estimated as $V_k/V_t \approx 4.3 \times 10^{-5}$, $V_k \approx 8.6 \times 10^{-10} \text{ m}^3 = 0.86 \text{ mm}^3$ and $R_k \approx 0.6 \text{ mm}$. The removal volume V_k is a complicated function of pulse and plasma parameters. Nevertheless, linear correlation between the rate constant (k) and pulse energy (Fig. 6) may be understood assuming that the density of the energy required to breakdown the antibiotic $w_v(\text{J/m}^3)$ is independent of the antibiotic concentration. Then $V_k = W(\tau)/w_v$, i.e. $k \propto V_k \propto W$.

Conclusions

The low voltage, low energy submerged pulsed arc can remove SDM efficiently from aqueous solutions. The rate constant for SDM decay was in the range of 0.13–1.9 min^{-1} for the studied pulse parameters, and linearly increased with pulse energy (inconsistency for 20 μ s pulses) and exponentially decreased with pulse duration. The energy E required for 90% SDM removal depended on the pulse parameters and was in the range of 1.6–114 kW-hr/m^3 .

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