Parameter optimization of ferro-sonication pre-treatment process for degradation of bisphenol A and biodegradation from wastewater sludge using response surface model

D.P. Mohapatra [a], S.K. Brar [a,*], R.D. Tyagi [a], R.Y. Surampalli [b]

[a] INRS-ETE, Université du Québec, 490, Rue de la Couronne, Québec, Canada G1K 9A9
[b] US Environmental Protection Agency, P.O. Box 17-2141, Kansas City, KS 66117, USA

ARTICLE INFO

ABSTRACT

In this study, the application of response surface model in predicting and optimizing the ferro-sonication pre-treatment for degradation of bisphenol A (BPA), an endocrine disrupter compound from wastewater sludge (WWS) was investigated. The ferro-sonication pre-treatment process was carried out according to central composite design (CCD) with four independent variables such as wastewater sludge solids concentration, pH, ultrasonication time and $FeSO_4$ concentration. The effect of ferro-sonication pre-treatment was assessed in terms of increase in sludge solids (suspended solids (SS) and volatile solids (VS)) and organic matter (chemical oxygen demand (COD) and soluble organic carbon (SOC)) solubilization and simultaneous BPA degradation from WWS. It was observed that among all the variables studied, ultrasonication time had more significantly affected the efficiency of the ferro-sonication pre-treatment process followed by $FeSO_4$ and solids concentration. Through this optimization process, it was found that maximum BPA degradation of 88% could be obtained with 163 min ultrasonication time, 2.71 mg/L $FeSO_4$ concentration, pH 2.81 with 22 g/L SS. Further, the effect of ferro-sonication pre-treatment on biodegradation of WWS was also studied. It was observed that ultrasonication time had significant effect and the higher biodegradation (32.48%) was observed at 180 min ultrasonication time.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Endocrine disrupting compounds (EDCs) have been found to cause adverse effects on the endocrine system of man and animals with particular environmental concern [1]. As better understanding of the biological effects of EDCs emerges, investigators have begun to study the potential effects of EDCs on human, which include malformations of newborns, undescended testicles, abnormal sperm, low sperm counts, abnormal thyroid function, breast cancer and testicular prostate cancer among others [2,3]. Bisphenol A (BPA) has been identified as EDC by the U.S. Environmental Protection Agency (EPA), World Wide Fund for Nature (WWF) and is declared as a social, environmental and global issue [4]. Recently, the report submitted by Canadian Health Measures Survey (CHMS) showed that Canadians aged 6–79 had a geometric mean concentration of urinary BPA of 1.16 μg/L. The report also showed that BPA was found in 91% of Canadians and higher concentrations were measured in teens aged 12–19 [5,6].

BPA is a representative EDC due to its large consumption as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester–styrene resins and flame retardants. Due to the daily use of these products, higher concentration of BPA is observed in wastewater (WW) and finally in wastewater sludge (WWS) (0.004–1.36 mg kg^{-1}) [4]. Many treatments, such as dewatering, digestion, burning, landfilling and use in agriculture have been carried out for the disposal of excess sludge. However, high cost of these treatments and presence of varied organic matter including BPA in sludge, makes its final disposal a challenge. Therefore, interest for solutions allowing sludge volume and mass reduction and simultaneous degradation of organic compounds has a great demand [7]. The effective removal of BPA from WWS is usually limited to physico-chemical pre-treatments, such as photo-catalytic oxidation, Fenton's oxidation, ultrasonication, ferro-sonication and ozonation [8–10].

Ferro-sonication pretreatment is a combination of ultrasonication and addition of $FeSO_4 \cdot 7H_2O$. Ultrasonic irradiation generates cavitation bubbles in medium, which repeats a cycle of formation, growth and collapse in accordance with ultrasonic waves. The induced cavitation that occurs during ultrasonication results in sudden and violent collapse of huge number of microbubbles, which generates powerful hydro-mechanical shear forces in the

---

bulk liquid surrounding the bubbles [11,12]. The high temperature produced during the bubble collapse (implosion) decomposes water (H_2O) into extremely reactive hydrogen atoms (H^+), and hydroxyl radicals (OH·) and in the cooling phase, these radicals will recombine to form hydrogen peroxide and molecular hydrogen [11,13]. Further, addition of $FeSO_4 \cdot 7H_2O$ results in higher production of OH· radicals due to the reaction between hydrogen peroxide and Fe^{2+}.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH \cdot + OH^- \tag{1}$$
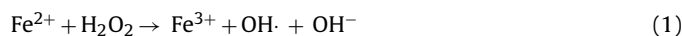
OH· radicals formed during ferro-sonication pre-treatment leads to oxidation and mineralization of organic compound present in WWS. However, no studies have been reported as yet on the degradation of BPA in WWS by ferro-sonication pre-treatment.

In fact, ferro-sonication would be a prospective method in augmenting sludge biodegradability for value-addition by solubilization of organic matter. To the best of our knowledge, none of the studies discussed the enhancement of biodegradability for sludge value-addition, such as production of biopesticides, bioplastics, enzymes, bioflocculants among others using ferro-sonication as pre-treatment.

Therefore, the objective of the present work is to study the optimization of ferro-sonication pre-treatment process to improve the solubilization, biodegradability and simultaneous degradation of BPA from WWS using response surface methodology.

2. Materials and methods

2.1. Chemicals

BPA (98% purity assay) was obtained from Sigma–Aldrich (Ontario, Canada). HPLC-grade methanol (MeOH), dichloromethane (DCM), acetone and chloroform, used for cleaning and extraction purposes, were purchased from Fisher Scientific (Ontario, Canada). Sep-Pak Plus C18 environmental cartridges used for solid phase extraction (SPE) clean-up was purchased from Waters (Milford, MA, USA). Acetic acid, hydrogen peroxide, sodium hydroxide and sulfuric acid were supplied by Fisher Scientific (Ontario, Canada) and were of analytical grade. HPLC grade water was prepared in the laboratory using a Milli-Q/Milli-RO Millipore system (Milford, MA, USA).

2.2. Wastewater sludge

Secondary sludge used in the study was collected from Quebec Urban Community (CUQ) wastewater treatment plant (Beauport, Quebec city, Quebec, Canada). Samples were collected in pre-cleaned amber glass bottles with aluminum foil-lined caps and stored under dark conditions at $4 \pm 1\,^\circ C$. The sludge suspended solids (SS) were concentrated from 1.5% (w/v) to higher SS concentrations by gravity settling and centrifugation of the settled sludge at $1600 \times g$ for 3 min in a Sorvall RC 5C plus Macrocentrifuge (rotor SA-600). The supernatant was discarded in order to obtain 15, 20, 25, 30 and 35 g/L SS.

2.3. Ferro-sonication pre-treatment of wastewater sludge

Ferro-sonication pre-treatment was carried out by addition of $FeSO_4 \cdot 7H_2O$ solution in WWS followed by ultrasonic pre-treatment. Four hundred milliliters of WWS was acidified to pH ranging from 2 to 4 by using 10 N H_2SO_4 and placed in a 1 L flask. The ultrasonication was carried out using ultrasonic homogenizer Autotune 750W (Cole-Parmer Instruments, Vernon Hills, IL, USA). The ultrasonication equipment was operated at a frequency of 20 kHz by using platinum probe with a tip diameter of 12 mm

and ultrasonic intensity of 15 W/cm². The ultrasonic intensity was defined as the actual power dissipated by the equipment divided by the area of the transducer. The ultrasonic probe was dipped in such a way that it was immersed 2 cm into the sludge.

2.4. Analysis

2.4.1. General

Analysis of pH, total solids (TS), suspended solids (SS), volatile solids (VS), soluble chemical oxygen demand (SCOD), soluble organic carbon (SOC) was carried out as per the standard methods [14]. The SS, VS, SCOD and SOC solubility increment were calculated as follows:

$$S_{ss} = \frac{SS_0 - SS_S}{SS_0} \times 100\% \tag{2}$$

$$S_{VS} = \frac{VS_0 - VS_S}{VS_0} \times 100\% \tag{3}$$

$$SCOD_{increment} = \frac{SCOD_S - SCOD_0}{TCOD} \times 100\% \tag{4}$$

$$SOC_{increment} = \frac{SOC_S - SOC_0}{TOC} \times 100\% \tag{5}$$

where, SS_0, VS_0, $SCOD_0$ and SOC_0 are referred to as the parameters of WWS before pre-treatment, and SS_S, VS_S, $SCOD_S$ and SOC_S are referred to as the parameters after pre-treatment.

2.4.2. BPA analysis

For quantification of BPA, the extraction was carried out by microwave assisted extraction method (MARS microwave extractor, CEM Corporation, NC, USA). Sep-Pak Plus C18 environmental cartridges were pre-conditioned by passing 7 mL of methanol and 3 mL of HPLC water at a flow rate of 1 mL min^{-1} [10]. LC–MS/MS analyses were performed on a TSQ Quantum Access (Thermo Scientific, Mississauga, Ontario) with a Finnigan surveyor LC pump equipped with a 120-vial capacity sample management system. The analytes were separated on a 3 μm, 100 mm × 2.1 mm Hypersil Gold C18 reverse phase column (Thermo Scientific, Peterborough). The sample injection volume was set at 10 μL. A binary mobile phase gradient with water [A] and methanol [B] was used for analyte separation at a flow rate of 200 μL min^{-1}. The gradient was performed as isocratic 5% A and 95% B for 6 min. The identification of BPA was done in a full-scan mode by matching the retention time and mass spectrum with true standards. Quantitative LC–MS/MS analysis was carried out in negative ionization (NI) condition and in selective reactions monitoring (SRM) mode using BPA d$_{16}$ as internal standard.

2.5. Response surface methodology

Application of response surface methodology for the optimization of ferro-sonication pre-treatment for degradation of BPA from WWS will help in overcoming the limitations of time consuming conventional optimization method of 'one factor-at-a-time' (at each step, a single factor is changed while other factors remain constant). Moreover, the statistical optimization method can evaluate the effective factors and help in building models to study interaction and select optimum conditions of variables for a desirable response. In the response surface method, the factors such as SS concentration (X_1), pH of sludge (X_2), $FeSO_4 \cdot 7H_2O$ concentration (X_3) and ultrasonication time (X_4) were considered as independent variables, and SCOD, SOC increment, biodegradability and BPA degradation in pre-treated sludge as dependent variables. To begin with, the screening experiments were carried out to determine the direction of optimal domain of each process. Two-level fractional factorial design (FFD) was employed in the

Table 1
Codes and values of experimental range of four variables for screening using response surface methodology.

Variables	Symbol	Coded level				
		−2	−1	0	+1	+2
Suspended solid (g/L)	X_1	15	20	25	30	35
pH	X_2	2.0	2.5	3.0	3.5	4.0
FeSO$_4$·7H$_2$O (mg/L)	X_3	1.46	1.95	2.43	2.92	3.41
Ultrasonication time (min)	X_4	60	90	120	150	180

screening step. Once the provisional optimal values were determined, a central composite design (CCD) was used to find the optimal conditions of these four factors (X_1, X_2, X_3 and X_4). In this regard, a set of 31 experiments including, 7 center points (0, 0, 0) and 7 axial points (+2, −2) and 17 points corresponding to a matrix of 2^3 which incorporate 17 experiments (+1, 0, −1) including four variables, were carried out. The levels of each factor along with their codes and values of two experimental designs are listed in Table 1. A multiple regression analysis of the data was carried out by STATISTICA 7 of STATSOFT Inc. (Thulsa, USA) by surface response methodology. After running the CCD experiments, a second-order polynomial regression equation was fitted to the data (Eq. (6)).

$$Y = \beta_0 + \sum_{i=1} \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j \qquad (6)$$

where, Y is predicted response of the dependent variable, X_i and X_j are independent variables influencing the response of Y, β_0 is constant of the second order equation, β_i is linear regression coefficient of each independent variable, β_{ii} is quadratic regression coefficient of each independent variable, and β_{ij} is regression coefficient of interactions between two independent variables. The significance of the second-order model as shown in Eq. (6) was evaluated by analysis of variance (ANOVA). The insignificant coefficient was eliminated after the F (Fisher)-test and the final model was obtained. Combination of factors (such as $X_i X_j$) represents an interaction between the individual factors in the respective term. The various response surface graphs presented are function of level of factors and indicate the effect of variables individually and in combination and determine their optimum level for solid and organic matter solubilization with simultaneous biodegradation and degradation of BPA from WWS. The response surface graphs presented the second-order polynomial model which showed the predicted response of two factors at a time, holding the other two factors at fixed zero level and are in fact more helpful in interpreting the main effect and the interactions.

2.6. Biodegradability test

Examination of biodegradability was carried out by inoculating the pre-treated and raw sludges with microbial consortia of 2% (v/v) of fresh activated wastewater sludge (1.5 mL) followed by incubation at $25 \pm 1\,°C$ at 150 rpm on a rotary shaker for 20 days. Oxygen corresponded to the oxygen entrained from the atmosphere into the shaking flasks on a rotary shaker. The biodegradability was assessed by the decrease in TS consumed by the microorganisms after incubation (20 days) (Eq. (7)). At the end of incubation, the volume loss due to evaporation was readjusted to 75 mL with Milli-Q water.

Biodegradability (%) =

$$\left(1 - \frac{\text{TS concentration after biodegradation}}{\text{TS concentration before biodegradation}}\right) \times 100 \qquad (7)$$

WWS pre-treatments rupture suspended solids (microbial cells), liberate the nutrients, partially solubilize the suspended solids, increase the soluble chemical oxygen demand, decrease viscosity and improve the overall WWS biodegradability [15,16]. Hence, in this research biodegradability was chosen as a parameter to assess the effectiveness of ferro-sonication pre-treatment process for value added products and simultaneous degradation of BPA.

3. Results and discussion

3.1. Screening experiments

The experimental results of screening experiments of ferro-sonication pre-treatment for studying the effect of solids concentration (X_1), pH (X_2), FeSO$_4$·7H$_2$O concentration (X_3), and ultrasonication time (X_4) on biodegradation and degradation of BPA are presented in Table 2. From the data presented, the higher response of BPA degradation and biodegradability was observed in trial no. 24 at ultrasonication time of 180 min, FeSO$_4$·7H$_2$O concentration of 2.43 mg/L at pH 3.0 and solids concentration 25 g/L. SS, VS and organic matter (SCOD and SOC) solubilization observed during trial no. 24 was 43.79%, 56.01%, 61.92% and 15.71%, respectively. BPA degradation and biodegradation observed during trial no. 24 was 82.99% and 32.48%, respectively. Higher degradation of BPA and increased biodegradation observed in trial no. 24 was due to higher SS, VS, SCOD and SOC solubilization. With the improvement of sludge solubilization during ferro-sonication pre-treatment process, organic matter will be transferred from solid to aqueous phase, which resulted in the increase in soluble protein and carbohydrate concentration in aqueous phase and decrease of SS, VS, SCOD and SOC in solid phase. Our previous study has demonstrated that increase in SS, VS, SCOD and SOC solubilization during hydrolysis and oxidative pre-treatment of WWS resulted in higher degradation of BPA [10].

The higher SS, VS, SCOD and SOC solubilization observed in trial no. 24 as compared to other trials was due to higher ultrasonication time leading to higher ultrasonication supplied energy. Higher energy input caused more acoustic cavitation in the medium, which then caused sludge floc disintegration and cell breakage leading to release of intracellular materials to aqueous phase [17,18]. Hence, at higher specific energy, solubilization started with the hydrolysis of carbohydrate followed by aminoacids and proteins and finally, fats and lipids and the subsequent phase where most of the organic matter was solubilized [18]. The higher ultrasonication time during trial no. 24 also leads to higher temperature which induced transformation of solid-state bound organic compounds into a soluble state.

The other reason for higher degradation of BPA observed in trial no. 24 might be due to higher production of OH· radicals with 180 min ultrasonication time. A comparative degradation of BPA (80.04%) was also observed in trial no. 22 with ultrasonication time of 120 min. In both trial no. 22 and 24, the pH and solids concentration of sludge was same with 3.4 mg/L and 2.43 mg/L FeSO$_4$·7H$_2$O concentration, respectively. The significant degradation of BPA in trial no. 22 with 120 min ultrasonication time compared to 180 min in trial no. 24 was due to the addition of higher concentration of FeSO$_4$, which enhanced the formation of OH· radicals in the solution (Eq. (1)) [19]. Taking into account the specific supplied energy (E), trial no. 22 was chosen as the best condition among the trials tested as it resulted in 39.62%, 52.03%, 56.01% and 14.78% SS solubilization, VS solubilization, SCOD and SOC increment, leading to 80.04% and 32.01% BPA degradation and biodegradation, respectively. Trial 22 was conducted at following conditions: 120 min ultrasonication time, 3.4 mg/L FeSO$_4$·7H$_2$O, pH 3 and 25 g/L of SS.

Table 2
Results of experimental plan by central composite design for changes in analytical parameters and simultaneous change in BPA degradation and biodegradability.

Trial	X_1	X_2	X_3	X_4	SSs (%)	VSs (%)	SCOD increment (%)	SOC increment (%)	BPA degradation (%)	Biodegradability (%)
1	20	2.5	1.95	90	14.37	26.89	32.56	8.0	24.59	8.01
2	20	2.5	1.95	150	33.10	51.10	54.11	14.19	71.36	14.93
3	20	2.5	2.92	90	14.89	26.89	32.01	8.4	33.4	11.18
4	20	2.5	2.92	150	33.81	51.19	53.91	14.86	78.21	22.05
5	20	3.5	1.95	90	14.05	22.17	28.75	7.51	22.99	6.49
6	20	3.5	1.95	150	32.11	49.87	44.16	11.99	67.55	13.56
7	20	3.5	2.92	90	19.07	22.19	28.11	7.5	26.38	6.67
8	20	3.5	2.92	150	33.52	46.73	44.85	11.27	71.93	13.0
9	30	2.5	1.95	90	16.13	25.51	26.75	8.10	18.77	7.98
10	30	2.5	1.95	150	35.19	38.13	52.14	13.71	60.49	19.56
11	30	2.5	2.92	90	16.18	25.97	27.21	8.17	21.56	6.19
12	30	2.5	2.92	150	35.19	38.64	56.95	13.99	68.73	24.10
13	30	3.5	1.95	90	13.97	18.55	23.71	9.10	18.73	8.32
14	30	3.5	1.95	150	33.52	45.92	45.76	14.73	54.47	13.56
15	30	3.5	2.92	90	14.15	23.33	24.11	9.11	32.61	6.77
16	30	3.5	2.92	150	32.19	47.59	56.93	14.70	61.11	24.45
17	15	3.0	2.43	120	34.72	49.63	51.11	17.11	69.73	19.76
18	35	3.0	2.43	120	28.11	41.05	43.01	13.56	53.16	14.18
19	25	2.0	2.43	120	27.34	52.71	46.92	15.78	57.9	17.01
20	25	4.0	2.43	120	28.75	48.11	51.03	13.11	53.11	18.96
21	25	3.0	1.46	120	36.19	49.71	43.78	14.49	49.72	13.3
22	25	3.0	3.4	120	39.62	52.03	56.01	14.78	80.04	31.01
23	25	3.0	2.43	60	9.19	17.11	20.18	8.23	14.93	6.11
24	25	3.0	2.43	180	43.79	56.01	61.92	15.71	82.99	32.48
25	25	3.0	2.43	120	34.26	46.8	48.11	13.99	71.58	14.53
26	25	3.0	2.43	120	34.10	46.39	48.0	13.99	71.03	14.22
27	25	3.0	2.43	120	34.26	46.8	48.92	12.51	69.73	14.69
28	25	3.0	2.43	120	34.26	46.77	48.57	13.47	71.68	14.01
29	25	3.0	2.43	120	34.29	46.58	48.19	12.14	71.05	14.22
30	25	3.0	2.43	120	34.00	46.07	48.77	12.83	71.0	14.37
31	25	3.0	2.43	120	34.33	46.62	48.52	13.27	71.6	14.09

3.2. Optimization studies

3.2.1. Effect of variables on BPA degradation

Using the method of experimental factorial design and response surface analysis, the optimal conditions to obtain higher degradation of BPA during ferro-sonication pre-treatment of WWS was determined. The validity of the model was proved by fitting different values of the variables into the model equation and carrying out the experiment at these values of the variables. The data were fitted into a second-order polynomial function (Eq. (6)). The statistical significance of the second-order polynomial model was verified by ANOVA. The quality of the model fit was evaluated by the coefficient R^2 which represents the proportion of variation in the response data and it can be explained by the fitted model. High R^2 was considered as an evidence for the applicability of the model in the range of variables included. It should be noted that an R^2 value greater than 0.75 indicates the aptness of the model. The analysis indicated that the second-order polynomial model resulted in a determination coefficient R^2 higher than 0.75, which ensured a satisfactory adjustment of the quadratic model to the experimental data.

The evaluation of statistical significance of four factors, such as solid concentration (X_1), pH (X_2), FeSO$_4$·7H$_2$O concentration (X_3) and ultrasonication time (X_4) and their interaction was based on probability (p) values. The regression model in terms of second-order polynomial model was fitted into the experimental data of BPA degradation. Analysis of variance (ANOVA) including the ratio of the level mean square (MS) and the residual MS followed a Fisher (F) distribution with degrees of freedom (df) are shown in Table 3. Except for linear effect of pH (X_2), all the main effects have MS higher than the residual MS which showed that most of the variation in the data of degradation of BPA is accounted by the separate effect of independent variables. The statistical significance of individual and interaction effects were also determined based on comparison of F-value (F) with critical F-value (F_c) at 95%, 99% and 99.9% confidence. Taking into account the effect of variables

on BPA degradation from WWS, solids concentration (X_1) showed significant linear effect ($F > F_c$ for probability $p < 0.05$) and highly significant quadratic effects ($F > F_c$ for probability $p < 0.01$); pH (X_2) showed no linear effect ($p > 0.05$), but showed highly significant quadratic effect ($F > F_c$ for $p < 0.01$); FeSO$_4$·7H$_2$O concentration (X_3) has highly significant linear effect ($F > F_c$ for $p < 0.01$) and significant quadratic effect ($F > F_c$ for $p < 0.05$); and ultrasonication time (X_4) had very highly significant linear and quadratic effect ($F > F_c$ for $p < 0.001$). In between combination of parameters, only FeSO$_4$·7H$_2$O concentration and ultrasonication time (X_3X_4) showed highly significant effects ($F > F_c$ for $p < 0.01$) on degradation of BPA from WWS.

The second-order polynomial regression equation (Eq. (6)) fitted well into the experimental data to give the following models (Eqs. (8)–(10)) including regression coefficients with coded terms of operational parameters for organic matter (COD and SOC) solubilization and BPA degradation. However, the regression coefficients which were found insignificant ($p > 0.05$) were excluded from the model.

$$Y_{SCOD} = -26.71 - 0.96X_1 - 0.06X_1^2 - 4.30X_2^2 + 0.8X_4 - 0.003X_4^2 \tag{8}$$

$$Y_{SOC} = -6.30 - 0.99X_2^2 + 0.35X_4 - 0.009X_4^2 \tag{9}$$

$$Y_{BPA} = -568.6 - 7.75X_1 - 0.17X_1^2 - 23.56X_2^2 - 78.37X_3$$
$$- 15.1X_3^2 + 3.3X_4 - 0.008X_4^2 - 0.01X_3X_4 \tag{10}$$

Hence, among all the four variables, ultrasonication time had very high significant effect on degradation of BPA from WWS followed by FeSO$_4$·7H$_2$O concentration, sludge solids concentration and pH. This could be explained by the fact that, higher ultrasonication time leads to: (i) increase of temperature within the medium

Table 3
ANOVA for the regression model equation and coefficients.

Model	BPA degradation					Biodegradability				
	SS	df	MS	F-test	p	SS	df	MS	F-test	p
X_1	360.66	1	360.663	5.7249	0.0293[*]	10.631	1	10.631	5.0285	0.0008[*]
X_1^2	554.79	1	554.787	8.8062	0.0090[*]	3.874	1	3.8740	0.1752	0.6810
X_2	39.81	1	39.813	0.6320	0.4382	12.472	1	12.472	0.5640	0.4635
X_2^2	991.93	1	991.932	15.7451	0.0011[*]	0.374	1	0.3737	0.0169	0.8981
X_3	545.09	1	545.091	8.6523	0.0095[*]	136.476	1	136.47	6.1721	0.0244[*]
X_3^2	362.40	1	362.401	5.7525	0.0290[*]	24.082	1	24.082	1.0891	0.3121
X_4	9240.34	1	9240.34	146.673	0.0000[*]	775.794	1	775.79	35.085	0.0000[*]
X_4^2	1619.64	1	1619.64	25.7089	0.0001[*]	1.300	1	1.2995	0.0587	0.8115
$X_1 X_2$	16.16	1	16.160	0.2565	0.6194	8.585	1	8.5849	0.3882	0.5419
$X_1 X_3$	4.14	1	4.143	0.0658	0.8008	0.333	1	0.3330	0.0150	0.9038
$X_1 X_4$	50.98	1	50.980	0.8092	0.3816	28.143	1	28.143	1.2727	0.2758
$X_2 X_3$	0.16	1	0.158	0.0025	0.9606	1.092	1	1.0918	0.0493	0.8269
$X_2 X_4$	42.64	1	42.641	0.6768	0.4227	7.508	1	7.5076	0.3395	0.5682
$X_3 X_4$	568.12	1	568.405	5.9640	0.0093[*]	29.988	1	29.987	1.3562	0.2612
Residual	1007.99	16	62.999	–	–	353.785	16	22.111	–	–

SS: sum of square; df: degrees of freedom; MS: mean square; p: probability.

[*] Significant values ($p < 0.05$).

resulting in thermal hydrolysis, (ii) higher solubilization of SS, VS and organic matters (SCOD and SOC), and (iii) higher formation of H_2O_2 due to bubble collapse and mixing effect resulting in higher production of OH· in the medium. As the ultrasonication time increased, organic matter (SCOD and SOC) solubilization and the number of OH· radicals in the medium increased leading to higher oxidation of BPA [20–22]. Similarly, Yan et al. [23] had observed that COD, organic matter and nitrogen solubilization increased with increasing ultrasonication time. The transformation of solid-state bound organic compounds into a soluble form could be induced continuously by the elevated bulk temperature during sonication. Higher ultrasonication time caused more acoustic cavitation in the medium, which then caused sludge floc disintegration and cell breakage leading to release of intracellular materials to aqueous phase. The cavitation threshold depends on the medium temperature, pressure, and ultrasonication time, among others [23].

Addition of $FeSO_4 \cdot 7H_2O$ during ferro-sonication pre-treatment of WWS enhanced the formation of OH· radicals in the solution. Hence, $FeSO_4 \cdot 7H_2O$ concentration had significant effect on degradation of BPA due to enhancement of higher production of OH· radicals during ultrasonication process. The hydroxyl radicals generated during ferro-sonication pre-treatment processes have an oxidizing potential of 2.8 V as compared to normal hydrogen electrode (NHE) and are capable of oxidizing a wide range of organic compounds including BPA in WW and WWS [24]. Ultrasonication is considered as a suitable method to improve the Fenton degradation of BPA [19,25,26].

The response surface graph of SCOD and SOC increment affected by the ultrasonication time and $FeSO_4 \cdot 7H_2O$ concentration at constant pH and solids concentration (Fig. 1a and b) showed that highest solubilization (61.92% and 15.71%, respectively) occurred at 180 min ultrasonication time and 2.43 mg/L $FeSO_4 \cdot 7H_2O$. BPA degradation from WWS assessed as a function of different ferrosonication pre-treatment operational parameters is presented in Fig. 2. The response surface graph of BPA degradation affected by the ultrasonication time and $FeSO_4 \cdot 7H_2O$ concentration at constant pH and solids concentration (Fig. 2a) showed that highest degradation (82.99%) occurred at 180 min ultrasonication time and 2.43 mg/L $FeSO_4 \cdot 7H_2O$. The results suggested that there was a correlation between organic matter solubilization and BPA degradation. Moreover, SCOD and SOC were mainly composed of soluble proteins and carbohydrates. Hence, at higher specific energy, solubilization started with the hydrolysis of carbohydrate followed by aminoacids and proteins and finally, fats and lipids and the subsequent phase where most of the organic matter was solu-
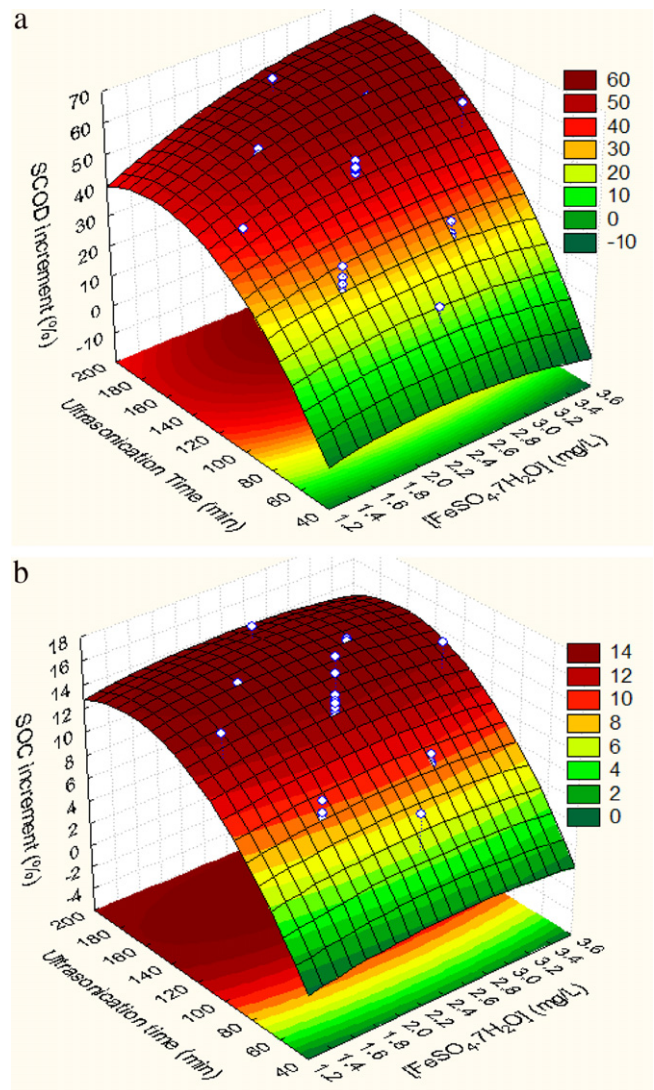

Fig. 1. Response surface plot of organic matter solubilization as a function of ultrasonication time and ferrous sulphate concentration: (a) COD solubilization, and (b) SOC solubilization.
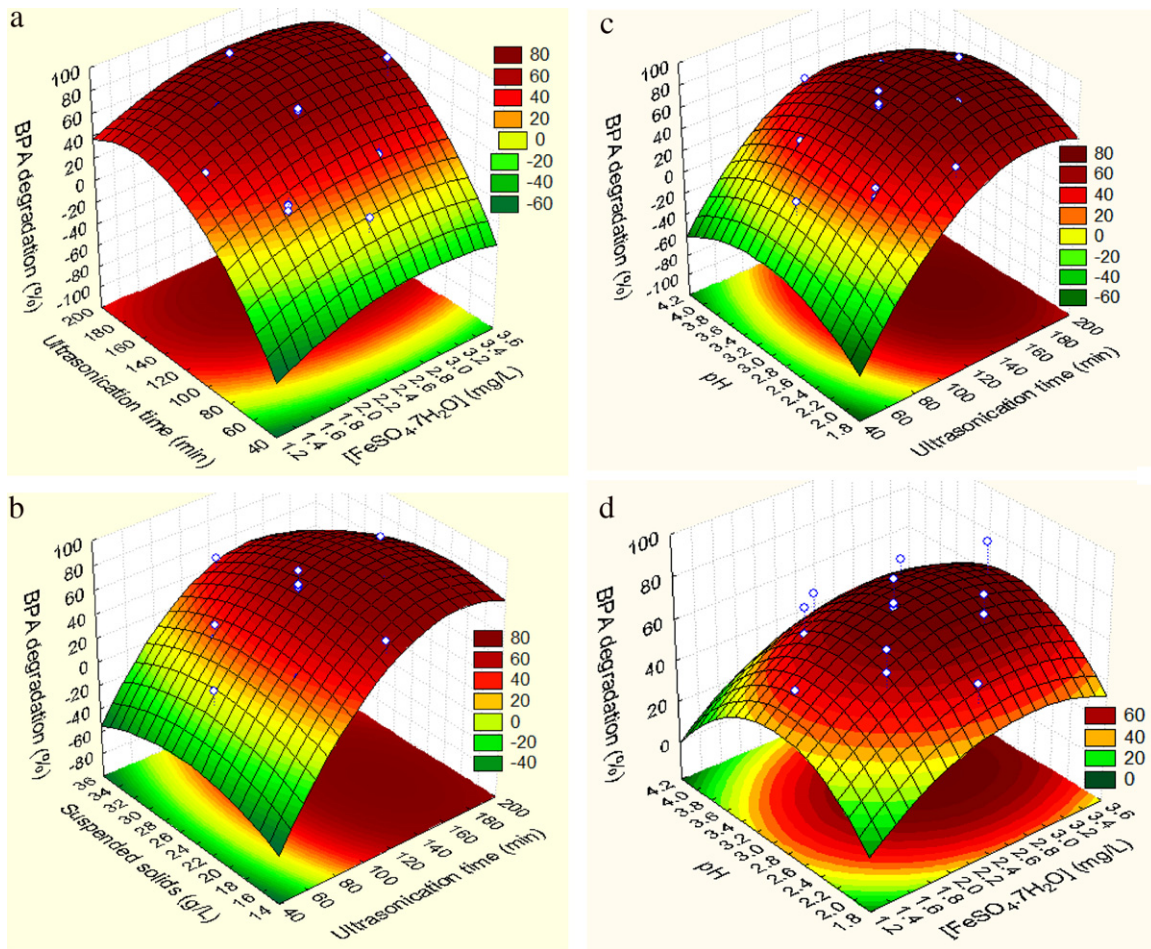
Fig. 2. Response surface plots of BPA degradation as a function of: (a) ultrasonication time and FeSO₄ concentration (pH and SS constant), (b) ultrasonication time and solids concentration (pH and FeSO₄ concentration constant), (c) ultrasonication time and pH (FeSO₄ concentration and SS constant) and (d) FeSO₄ concentration and pH (ultrasonication time and SS constant).

bilized. Therefore, higher degradation of BPA from WWS during higher ultrasonication time and FeSO₄·7H₂O concentration was due to higher production of OH· radicals and solubilization of sludge organic matter (COD and SOC).

Other factors that showed significant effect on BPA degradation from WWS were solids concentration and quadratic effect of pH. Fig. 2b shows the response for the interactive factors, solids concentration (X_1) and ultrasonication time (X_4), when pH and FeSO₄·7H₂O concentration were fixed at central point. Higher BPA degradation (80%) was obtained in the range of 20–25 g/L SS and 120–180 ultrasonication time. The same response could be predicted in the range of 120–180 min ultrasonication time and 2.5–3.5 pH at constant solids and FeSO₄·7H₂O concentration (Fig. 2c). This can be explained by the fact that, due to high octanol–water partition coefficient (log K_{ow} = 2.3–3.82) and hydrophobic nature [27], BPA has the tendency to strongly associate with the solids. The initial BPA concentration was observed in wastewater sludge with five solids (X1) concentrations such as 15, 20, 25, 30 and 35 g/L. Trials were carried out with different parameters (X1, X2, X3 and X4) and the final BPA concentration was observed to determine the % BPA degradation. Higher concentration of BPA was observed with increasing solids concentration [10]. Increased ultrasonication time leads to increase in hydro-mechanical shear force within the medium resulting in dissociation of solids and organic matter so that the adsorbed BPA was released to the aqueous phase. As the size of the flocs decreased with increasing ultrasonication

time, overall availability of sorbed BPA molecules to react with OH· radicals increased resulting in higher degradation of BPA.

Fig. 2d shows the response for the interactive factors, FeSO₄·7H₂O concentration (X_4) and pH (X_2), when ultrasonication time and solids concentration was fixed at central point. This suggested that, pH and FeSO₄·7H₂O concentration lower than 2.2 and 1.6 mg/L respectively, produced less effect on degradation of BPA from WWS. Higher degradation of BPA (>60%) was obtained at pH 2.6–3.8 and 2.0–3.2 mg/L FeSO₄·7H₂O concentration. This can be explained by the fact that FeSO₄·7H₂O concentration lower than 2 mg/L was not sufficient to release large amount of iron ions to react with H₂O₂ produced during ultrasonication and form reactive OH· radicals that lead to BPA degradation. Ioan et al. [19] observed more than 80% of degradation of BPA at 2.5 mg/L FeSO₄·7H₂O concentration and pH 4. However, when the pH increased to the range of 4.5–6.5 and FeSO₄·7H₂O concentration decreased to 1.4 mg/L, BPA degradation decreased below 30%. Hence, a relative FeSO₄·7H₂O concentration reduces the efficiency of the process by regulating the production of OH· radicals (Eq. (1)) that leads to BPA degradation.

Therefore, ferro-sonication pre-treatment process with chosen parameters can be considered an oxidation process that played a vital role in enhancement of solubilization of sludge solids and organic matter and simultaneous degradation of BPA from WWS. From the model based on response surface methodology, the optimal conditions of ferro-sonication pre-treatment of secondary

sludge at 15 W/cm^2 ultrasonication intensity were identified as follows: 163 min ultrasonication time, 2.71 mg/L FeSO$_4$·7H$_2$O concentration, pH 2.81 with 22 g/L SS, to obtain a maximum 88% of BPA degradation from WWS.

3.2.2. Effect of variables on biodegradation

WWS solids (SS and VS) and organic matter (COD and SOC) solubilization has been adopted as a measure of ferro-sonication pre-treatment efficiency to improve biodegradability. As shown in Table 3, solid concentration (X_1) and ultrasonic time (X_4) showed very highly significant linear effect ($p < 0.001$); FeSO$_4$·7H$_2$O concentration (X_3) showed significant linear effect and other factors showed no effect on biodegradation. Combination of parameters of ferro-sonication pre-treatment process did not show any interaction effect on biodegradability. The regression coefficients were than fitted in Eq. (6) to give the following model (Eq. (11)).

$$Y_{\text{Biodegradability}} = -1.32X_1 - 23.63X_3 - 0.18X_4 \qquad (11)$$

The above analysis of significance of the factor on response of biodegradability showed that ultrasonication time exhibited major effect on improving the biodegradability followed by solids concentration and FeSO$_4$·7H$_2$O concentration. This can be explained by the fact that, increase in ultrasonication time leads to increase in power input resulting in higher disintegration of sludge solids and organic matter. The disintegration degree of sonicated sludge increased significantly with increasing specific energy [17,28]. In fact, under powerful hydro-mechanical shear forces generated from sudden and violent collapse of microbubbles, extracellular polymeric substances (EPS) considered as matrix that is embedded in cell sludge was degraded [29]. Consequently, the organic matter contained in EPS and cells was solubilized, coming under attack of collapsing cavitation bubbles and increasing the tendency to augment biodegradability.

The response surface plots in Fig. 3 presented the predicted biodegradability by using the four combinations of ferro-sonication pre-treatment process. As shown in Fig. 3a, 30% of biodegradability was achieved with ultrasonic time more than 120 min and 50% can be achieved by increasing the ultrasonication time more than 200 min. While pH and FeSO$_4$·7H$_2$O concentration were fixed at central point, highest biodegradability of 30% was obtained in the range of 20–25 g/L SS and 120–160 min ultrasonication time (Fig. 3b). The effective impact of the lower solids concentration on biodegradation of sludge was also in agreement with the results of Verma et al. [30] who reported the optimal SS concentration as 20 g/L for the biodegradability of alkaline thermal hydrolyzed sludge to produce *Trichoderma viride* based biopesticides. At higher solids concentration, the microorganisms could be inhibited by higher amount of substrate and limited mass and oxygen transfer (oxygen inhibition effect/substrate inhibition effect).

4. Conclusions

The present research work on ferro-sonication pre-treatment of secondary sludge for degradation of bisphenol A from wastewater sludge and enhancement of biodegradability led to following conclusions:

1. The second-order response surface model was adequate to predict the bisphenol A degradation and biodegradability enhancement from wastewater sludge within four independent variables namely, solids concentration, pH, FeSO$_4$·7H$_2$O concentration and ultrasonication time.
2. All the four independent variables showed significant effect on degradation of bisphenol A from wastewater sludge. Ultrasonication time plays an important role for increase in sludge solids (SS and VS) and organic matter (COD and SOC) solubilization and OH· radicals production in the medium for degradation of bisphenol A.
3. The optimal conditions developed by the response surface model in order to obtain maximum 88% of bisphenol A degradation from wastewater sludge by ferro-sonication pre-treatment were as follows: 163 min ultrasonication time, 2.71 mg/L FeSO$_4$·7H$_2$O concentration, pH 2.81 at 22 g/L SS.
4. Ultrasonication time and solids concentration showed significant effect on biodegradability enhancement of wastewater sludge. Higher biodegradability (32.48%) was observed at 180 min and 25 g/L ultrasonication time and solid concentration, respectively.
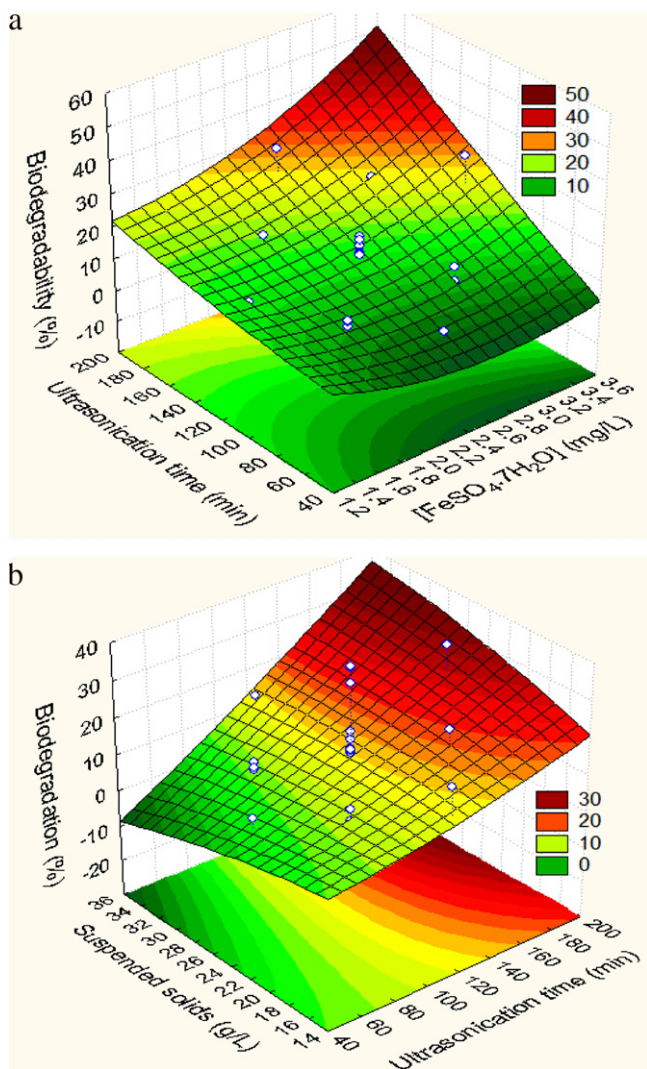
Acknowledgements

Fig. 3. Response surface plots of biodegradability as a function of: (a) ultrasonication time and FeSO$_4$ concentration (pH and SS constant), (b) ultrasonication time and solids concentration (pH and FeSO$_4$ concentration constant).

References

[1] K.L. Thorpe, T.H. Hutchinson, M.J. Hetheridge, M. Scholze, J.P. Sumpter, C.R. Tyler, Assessing the biological potency of binary mixtures of environmental estrogens using vitellogenin induction in juvenile rainbow trout (*Oncorhynchus mykiss*), Environ. Sci. Technol. 35 (2001) 2476–2481.

[2] C.A. Kimmel, Approaches to evaluating reproductive hazards and risks, Environ. Health Perspect. 101 (Suppl. 2) (1993) 137–143.

[3] F.S. Vom Saal, S.C. Nagel, B.G. Timms, W.V. Welshons, Implications for human health of the extensive bisphenol A literature showing adverse effects at low doses: a response to attempts to mislead the public, Toxicology 212 (2–3) (2005) 244–252.

[4] D.P. Mohapatra, S.K. Brar, R.D. Tyagi, R.Y. Surampalli, Physico-chemical pre-treatment and biotransformation of wastewater and wastewater sludge-Fate of bisphenol A, Chemosphere 78 (2010) 923–941.

[5] Statistics Canada, Canadian Health Measure Survey: Lead, bisphenol A and mercury. http://www.statcan.gc.ca/daily-quotidien/100816/dq100816a-eng.htm, 2010 (16.07.10).

[6] CBC news, Contaminated Canadians: BPA found in 91% of Canadians. http://cosmos.bcst.yahoo.com/up/player/popup/index.php?rn=222561&cl=21427837&ch, 2010 (11.07.10).

[7] T.I. Yoon, H.S. Lee, C.G. Kim, Comparison of pilot scale performances between membrane bioreactor and hybrid conventional wastewater treatment systems, J. Membr. Sci. 242 (1) (2004) 5–12.

[8] M. Deborde, S. Rabouan, J.P. Duguet, B. Legube, Kinetics of aqueous ozone induced oxidation of some endocrine disruptors, Environ. Sci. Technol. 39 (2005) 6086–6092.

[9] M.J. Zhan, X. Yang, Q.M. Xian, L.R. Kong, Photosensitized degradation of bisphenol A involving reactive oxygen species in the presence of humic substances, Chemosphere 63 (2006) 378–386.

[10] D.P. Mohapatra, S.K. Brar, R.D. Tyagi, R.Y. Surampalli, Degradation of endocrine disrupting bisphenol A during pre-treatment and biotransformation of wastewater sludge, Chem. Eng. J. 163 (2010) 273–283.

[11] S.K. Khanal, M. Montalbo, J. Van Leeuwen, G. Srinivasan, D. Grewell, Ultrasound enhanced glucose release from corn in ethanol plants, Biotechnol. Bioeng. 98 (5) (2007) 978–985.

[12] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods, Adv. Environ. Res. 8 (2004) 553–597.

[13] A. Tiehm, K. Nickel, M. Zellhorn, U. Neis, Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, Water Res. 35 (8) (2001) 2003–2009.

[14] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.

[15] S. Barnabe, Hydrolyse et oxidation partielle des boues d'epuration pour la production de *Bacillus thuringiensis* HD-1. Ph.D. thesis, INRS-ÉTÉ, Universite de Quebec, Quebec, Canada, 2004, pp. 233.

[16] T.T.H. Pham, S.K. Brar, R.D. Tyagi, R.Y. Surampalli, Ultrasonication of wastedwater sludge-Consequences on biodegradability and flowability, J. Hazard. Mater. 163 (2–3) (2009) 891–898.

[17] C. Bougrier, H. Carrere, J.P. Delgenes, Solubilization of waste-activated sludge by ultrasonic treatment, Chem. Eng. J. 106 (2005) 163–169.

[18] S. Pilli, P. Bhunia, S. Yan, R.J. LeBlanc, R.D. Tyagi, R.Y. Surampalli, Ultrasonic pre-treatment of sludge: a review, Ultrason. Sonochem. 18 (2011) 1–18.

[19] I. Ioan, S. Wilson, E. Lundanes, A. Neculai, Comparision of Fenton and sono-Fenton BPA degradation, J. Hazard. Mater. 142 (2007) 559–563.

[20] R.A. Torres, F. Abdelmalek, E. Combet, C. Petrier, C. Pulgarin, A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters, J. Hazard. Mater. 146 (2007) 546–551.

[21] M. Inoue, Y. Masuda, F. Okada, A. Sokurai, I. Takahashi, M. Sakakibara, Degradation of BPA using sonochemical reactions, Water Res. 42 (2008) 1379–1386.

[22] Z. Guo, R. Feng, Ultrasonic irradiation-induced degradation of low concentration bisphenol A in aqueous solution, J. Hazard. Mater. 163 (2009) 855–860.

[23] Y. Yan, L. Feng, C. Zhange, H. Zhu, Q. Zhou, Effect of ultrasonic specific energy on waste activated sludge solubilization and enzyme activity, Afr. J. Bitechnol. 9 (12) (2010) 1776–1782.

[24] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243.

[25] R.A. Torres, C. Petrier, E. Combet, F. Moulet, C. Pulgarin, Bisphenol A mineralization by integrated ultrasound–UV–iron (II) treatment, Environ. Sci. Technol. 41 (1) (2007) 297–302.

[26] R.A. Torres, G. Sarantakos, E. Combet, C. Petrier, C. Pulgarin, Sequential helio-photo-Fenton and sonication processes for the treatment of bisphenol A, J. Photochem. Photobiol. A: Chem. 199 (2–3) (2008) 197–203.

[27] C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, L.R. Hariis, A review of the environmental fate, effects, and exposures of bisphenol A, Chemosphere 36 (1998) 2149–2173.

[28] M.R Salsabil, A. Prorot, M. Casellas, C. Dagot, Pre-treatment of activated sludge: effect of sonication on aerobic and anaerobic digestibility, Chem. Eng. J. 148 (2009) 327–335.

[29] E. Neyens, J. Baeyens, R. Dewil, B. De Heyder, Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, J. Hazard. Mater. 106B (2004) 83–92.

[30] M. Verma, S.K. Brar, A.R. Riopel, R.D. Tyagi, R.Y. Surampalli, J.R. Valero, Pre-treatment of wastewater sludge-biodegradability and rheology study, Environ. Technol. 28 (2007) 273–284.