

Research Article

Removal of 17 β -Estradiol (E2) from Aqueous Solutions Using Potassium Permanganate Combined with Ultraviolet (KMnO₄/UV)

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17 β -Estradiol (E2) has a significant health risk to humans, even at the ng/L level, and is discharged to the aqueous environment through wastewater. Advanced oxidation processes were proposed as an efficient process for the removal of E2. In this study, a combination of ultraviolet-C (UV-C) and KMnO₄ was applied for the removal of E2. Results have shown that the removal efficiency of E2 in pH 4 (acidic condition) was 93.80 \pm 0.42%. But, removal efficiency in neutral (7) and alkaline (10) conditions was 78.3 \pm 2.12% and 84 \pm 0.71%, respectively. The effect of Fe⁺², Ca⁺², Mg⁺², Mn⁺², and Fe⁺³ ions (1 mg/L) was investigated in optimized pH (4). Mn⁺², Fe⁺², and Ca⁺² ions enhanced the removal efficiency to 94.8 \pm 0.84%, 95.55 \pm 0.07%, and 94.7 \pm 0.14%, respectively ($p > 0.05$), while Mg⁺² and Fe⁺³ ions decreased the removal efficiency significantly to 76.15 \pm 1% and 83.91 \pm 0.3% ($p < 0.05$). The efficiency of E2 removal in the presence of 5 mg/L of PAC reduced significantly to 85 \pm 4.24% ($p < 0.05$). Also, humic substances like humic acid, fulvic acid, and a combination of them could enhance the efficiency to 99.87 \pm 0.01%, 99.9 \pm 0.06%, and 99.93 \pm 0.014%, respectively ($p > 0.05$). The result indicates that the rate of oxidation of E2 is related to the second exponent of the initial concentration of E2 for optimum pH and the presence of all ions. But, in the presence of humic substances, the first-order kinetic reaction was best applicable in describing oxidation of E2. Removal of chemical oxygen demand for E2 after 120 minutes' of contact time at optimum pH (86 \pm 4.2%) demonstrated mineralization of these compounds at acceptable levels. Results presented that the UV-C/KMnO₄ process is efficient for the removal of hormones from the aqueous solution.

1. Introduction

Endocrine-disrupting compounds (EDCs) are considered as micropollutants that can cause widespread environmental damages [1]. EDCs can cause genital disorders and subsequently reduction in the number of sperms in wildlife [2]. Release of wastewater including the metabolism of humans and herd of livestock (excrement and urine) is the main natural source of estrogen which enters the aquatic environment, while the synthetic source of estrogen comes from effluent factories, which produce medicines like oral contraception drugs [3]. The most important natural and anthropogenic EDCs are 17 β -estradiol (E2), 17 α -ethynylestradiol (EE2), and biphenyl A (BPA) [4]. E2 has high endocrine-disrupting activity at ng/L levels and is regarded as a toxic and powerful intracellular estrogen [5]. Based on the

reports, E2 is excreted by adult male, women, and pregnant women about 1.83, 2.40, and 277 μ g/d/person, respectively [6]. Different investigations showed that standard wastewater treatment systems cannot eliminate these compounds, and therefore new methods should be established for the treatment of them [7]. However, most research studies are emphasized on the usage of photochemical processes, especially advanced oxidation processes (AOPs) [8]. One of the most important elements of photochemical processes is light. Observable or ultraviolet radiation can provide the conditions for a chemical reaction and act selectively. In these processes, chemical bands destruct and produce compounds with the simpler structure [8]. The main characteristic of AOPs is the production of extremely active species like hydroxyl radicals (OH), which can oxidize a wide range of pollutants non-selectively and fast [7]. Application of titanate nanotubes

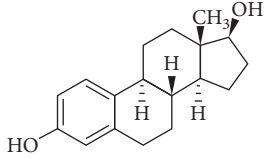
(TNTs@AC) with ultraviolet rays to remove estradiol in the aqueous medium is one of the methods of AOP that has shown high removal efficiency [9]. Also, in a study performed on the removal of ciprofloxacin using the same nanotube, good efficiency was observed [10]. 2D/1D graphic carbon nitride hybridized with titanate nanotubes (g-C₃N₄/TNTs) is another method used to remove sulfamethazine and showed high efficiency. Due to the good efficiency of hybrid methods, this method is known as an efficient method, but a suitable catalyst has always been discussed [11]. Potassium permanganate (KMnO₄) has adequate effects on the removal of phenolic substances [12]. Some interesting properties of potassium permanganate (KMnO₄) oxidation are the easiness of management, relative stability, comparatively inexpensive, moderate oxidation property, and easy to be combined with other traditional water treatment processes [12]. Individual application of each oxidant has low efficiency in E2 removal [3, 13]. Thus, combining UV and KMnO₄ as a promising method in the removal of E2 was investigated in the present study. In this research, experiments were conducted to determine the reaction kinetics and removal of E2 by the KMnO₄/UV system. The impact of environmental conditions (pH and contact time) and the presence of cosolutes, e.g., humic acid (HA), fulvic acid (FA), and their combination, polyaluminum chloride, CaCl₂, MgCl₂, MnCl₂, FeCl₂, and FeCl₃, were assessed. Also, the chemical oxygen demand (COD) was examined.

2. Materials and Methods

2.1. Reagents and Chemicals. 17 β -Estradiol (E2) (>99% purity) and potassium permanganate (KMnO₄) (98% purity) were purchased from Sigma-Aldrich (USA). Table 1 shows the characteristics of E2 [6]. Calcium chloride (CaCl₂), magnesium chloride (MgCl₂), manganese chloride (MnCl₂), iron II chloride (FeCl₂), iron III chloride (FeCl₃), and polyaluminum chloride (PAC) (Al₂(OH)_nCl_{6-n}) were purchased from Merck (Germany). Also, methanol, tetra-butanol, acetonitrile, and acetone of HPLC grade and humic and fulvic acid were purchased from Sigma-Aldrich (USA). Other chemicals were in analytical grade.

2.2. Removal Experiments and Analysis. Stock solution of E2 (100 mg/L) was made in acetonitrile and protected from light using an amber glass bottle (250 mL) that was covered with aluminum foil and then kept in the refrigerator at 4°C. The ideal concentration of E2 (1 mg/L) was prepared by dilution of the stock solution. Also, 10 mL of the stock solution of KMnO₄ was freshly prepared (100 mg/L) and used for experiments. A reactor (cylinder shape) was used for experiments. In each experiment, 250 mL of the solution containing 1 mg/L of E2 and 2 mg/L of KMnO₄ was poured into the reactor. pH was adjusted by HCl (1 M) and NaOH (1 M). A UV-C lamp (6 W, $\lambda = 254$ nm) was put in the cylindrical reactor and placed on a magnet stirrer. The solution was mixed by the magnetic stirrer. Effect of different ions like Fe⁺³, Ca⁺², Mg⁺², Fe⁺², and Mn⁺² (1 mg/

TABLE 1: Characteristics of estradiol.

Structure	
Molecular formula	C ₁₈ H ₂₄ O ₂
Melting point (°C)	178–179
Molecular weight	272.4
LogK _{ow}	3.94
pKa	10.6
Vapor pressure	3 × 10 ⁻⁸
Solubility (mg/L)	13

L) in the form of chloride salts; HA, FA (10 mg/L), and the combination of HA + FA; and also Al⁺³ by adding PAC (5 mg/L) to the reactor on the removal of E2 was studied. Removal of E2 in the UV/KMnO₄ process was evaluated based on the following equation:

$$\text{removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

where C_i and C_f are the initial and final concentrations of E2 (mg/L).

2.3. Kinetic Analysis. The kinetics of E2 oxidation were investigated using zero-, first-, and second-order kinetic models for all factors. The three kinetic models are presented in the linear forms by equations (2)–(4), respectively,

$$C_t = C_i - k_0 t, \quad (2)$$

$$\ln C_t = \ln C_i - k_1 t, \quad (3)$$

$$\frac{1}{C_t} = \frac{1}{C_0} - k_2 t, \quad (4)$$

where k_0 is the zero-order oxidation rate constant (mg/L.min) and achieved from the slope of the plot of C_t versus t , k_1 is the first-order oxidation rate constant (1/min) and achieved from the slope of the plot of $\ln C_t$ versus t , k_2 is the second-order oxidation rate constant (L/mg.min) and achieved from the slope of the plot of $1/C_t$ versus (t), C_t is the remaining concentration of E2 in the solution (mg/L), and C_0 is the initial concentration of E2 in the solution (mg/L) at time t . However, regression coefficients (R^2) were estimated from the plots. Finally, equations with the greatest R^2 were chosen as the best model for describing the kinetics of E2 oxidation. After that, the half-life ($t_{1/2}$) (min) for pseudo-zero, first, and second order of E2 oxidation was calculated using the following equations [14, 15]:

$$t_{1/2} = \frac{C_0}{2k}, \quad (5)$$

$$t_{1/2} = \frac{(\ln 2)}{k}, \quad (6)$$

$$t_{1/2} = \frac{1}{kC_0} \quad (7)$$

2.4. Statistical Analysis. The average values and standard deviations were calculated using Excel (Microsoft Corporation). Statistical analysis was performed with SPSS Statistics for Windows, Version 16. Significant difference between experimental treatments was analyzed using one-way analysis of variance (ANOVA) and independent samples and paired sample *t*-tests with a 95% confidential interval (*p* value < 0.05).

2.5. Analytical Method

2.5.1. HPLC Analysis. At intervals of the E2 concentration reaction, the samples were examined by HPLC equipped with a UV detector at a wavelength of 280 nm. The reverse-phase C-18 column was used as the fixed phase (C-18 column, 150 mm, and 4.6 mm), and the mobile phase was the water-sterile mixture (50/50, vol/vol) with a flow rate of 1.0 ml per minute. The sample injection volume was 20 μ L. Errors were below 5%.

2.5.2. COD Measurement. Chemical oxygen demand (COD) was measured using the closed-reflux titrimetric method (standard methods) (APHA, 2005). Chemical oxygen demand of the solution was measured before and after treatment by the UV/KMnO₄ process at time sampling. Distilled water was used as the blank sample. The COD removal was determined as follows:

$$\text{COD removal (\%)} = \frac{(A - B) \times N \times 1000 \times 8}{\text{volume of sample (ml)}}, \quad (8)$$

where *A* is the volume of FAS (mL) that was consumed for the blank sample, *B* is the volume of FAS used for the tested samples, *N* is the normality of FAS (0.01 N), and 8 is the milliequivalent weight of oxygen [16].

3. Results and Discussion

3.1. Effect of pH on the Removal of E2. pH has a considerable effect on the removal of E2 by the UV/KMnO₄ process. Figure 1 represents the percentage of removal efficiency at acidic, neutral, and basic pH (4, 7, and 10) for 1 mg/L of E2 with UV-C + KMnO₄ (2 mg/L). Removal efficiency increased when pH decreased. The maximum and minimum removal efficiencies were obtained at pH 4, 93.8 \pm 0.42%, and pH 10, 78.3 \pm 2.12%. The efficiency of the neutral condition was 84 \pm 0.71%. It should be noted that removal of E2 at pH 4 was faster than other values. More than 80% of E2 removed was within 40 min and then reached to 93.8% \pm 0.42 within 120 min. Under UV irradiation, water molecules can produce hydrated electrons (e⁻_{aqu}), OH \bullet , H⁺, and H \bullet (equation (9)) [17]:

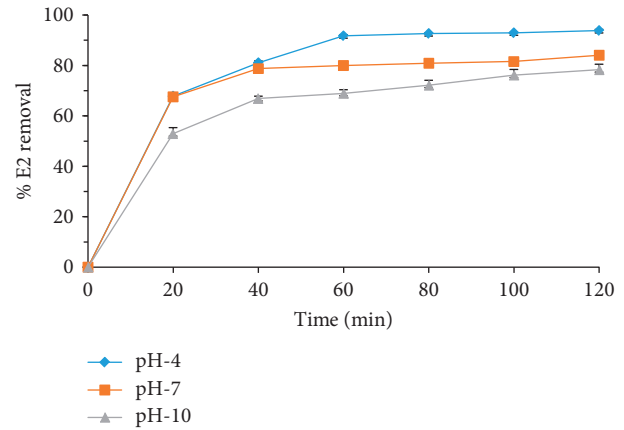
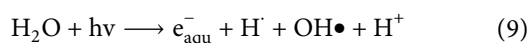
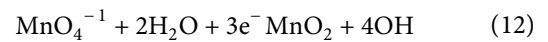
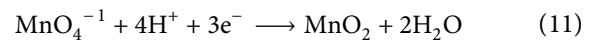
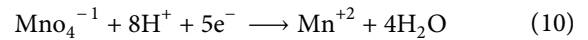
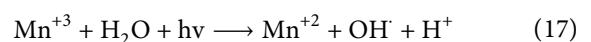
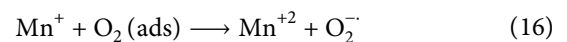
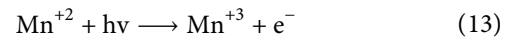


FIGURE 1: Removal percentage of E2 in different pH.

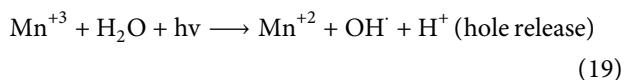
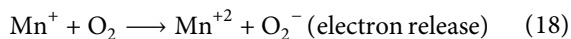
pH is a significant factor in the oxidation process by permanganate because it affects the redox potential of the system [18]. The number of electrons exchanged in the oxidation process is affected by the oxidation potential. Based on the study by Yan and Schwartz, the prominent reaction in highly acidic condition is as the same as the mentioned process in equation (10). Between pH 3 and 12, permanganate can exchange three electrons [19]. Reaction 11 occurs in acidic conditions ($E^\circ = +1.70$ V), and reaction 12 occurs in alkaline and neutral conditions ($E^\circ = +0.59$ V) [15]:



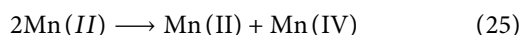
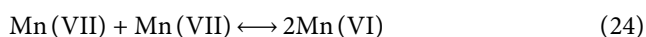
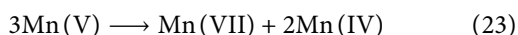
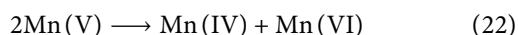
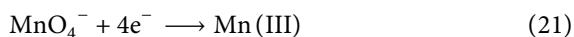
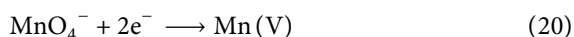
Acidic solutions have a higher oxidation potential (E°) than the alkaline solutions. Therefore, the reaction medium affects the oxidation mechanism. Finally, in the presence of KMnO₄, the reduction of MnO₂ to Mn⁺² leads to E2 removal from water. But, the combination of the two methods of removing by potassium permanganate and ultraviolet light changed the removal mechanism. Photodegradation on Mn⁺² can be represented by the following mechanism:



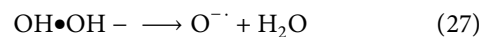
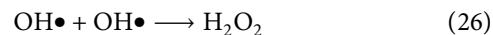
Since Mn³⁺ and Mn⁺ ions are relatively unstable as compared to Mn²⁺ ions (ads), there is tendency for the transfer for the trapped charges from Mn³⁺ and Mn⁺ to the interface to initiate the following reactions (described by equations (18) and (19)):



The photogenerated superoxide ion (O_2^-) and hydroxyl radical (OH^\bullet) are highly reactive and can effectively degrade E2. According to its pK_a of 10.71 [20], E2 existed in the neutral form within the experimental pH range. In a study by Haodong et al., to identify key reactive species involved in the photocatalytic degradation process, they conducted a series of cooling experiments such as $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and hole (h^+), respectively. In general, the hole can directly oxidize the organic compound and be involved in the formation of ROS (e.g., $\bullet\text{OH}$ and H_2O_2) [11]. As mentioned in the contaminant removal mechanisms by KMnO_4 , acidic solutions have a higher oxidation potential (E°) than the alkaline solutions. Mn (VII) can reduce to different types of oxidizers in acidic, alkaline, and neutral conditions like Mn (VI), Mn (V), Mn (IV), Mn (III), and Mn (II). The pH and nature of the reactant may be related to the activity of these mediating oxidants. In the acidic condition, the potential of standard redox for Mn (VII)/Mn (IV), Mn (VII)/Mn (II), Mn (III)/Mn (II), and Mn (VI)/Mn (III) is 1.69, 1.51, 1.51, and 0.95 V, respectively, at 25°C [20]. The role of reactive manganese intermediates cannot be ignored because they can enhance the degradation of organic compounds (e.g., phenolic compounds). Among these forms of manganese, manganese (VI) and manganese (III) can only exist in very acidic or alkaline conditions, indicating that they are not favorable to the removal of E2 in the present study. In weakly acidic conditions, manganese (V), manganese (VI), and manganese (III) are relatively unstable and disproportionate (described by equations (20)–(25)). Therefore, even if they have strong oxidation ability in acidic conditions, their role in oxidation cannot be ignored. The formation of MnO_2 during permanganate oxidation is important for organic compounds' degradation because many studies have shown that MnO_2 could remove many xenobiotic pollutants in laboratory scale [21]:



Alkaline conditions, on the other hand, significantly reduce the removal efficiency of E2 due to the reaction of hydroxyl radicals with each other (equation (26)) (as well as the scavenging effect from OH^- (equation (27)):



Furthermore, an alkaline pH affects the redox potential (E°) of OH^\bullet by decreasing it approximately by 18% [21]. Xu et al. examined the destruction of 17β -estradiol (E2) by MnO_2 at different pH levels and showed that the efficiency increased with decreasing of pH of MnO_2 activity due to more favorable conditions for the formation of surface precursor complexes [20]. Aleboye et al. evaluated the oxidation of azo dyes with permanganate. They have reported that the acidic condition has a positive effect on the reaction and the rate of azo dye degradation is dependent on pH over the range of pH 1–7 [18]. The results of these studies are consistent with our observations.

It is obvious from Table 2 that the second-order reaction had a relatively high linearity with a high correlation coefficient (R^2) 0.932. Zero- and first-order kinetic models had low correlation coefficients (R^2) 0.603 and 0.84, respectively. It can be concluded that the second-order kinetic reaction was the best model in describing oxidation of E2. The result indicates that the rate of oxidation of E2 is related to the second exponent of the initial concentration of E2. Increasing the concentration of E2 leads to an increase in the rate of oxidation.

3.2. Effect of Coexisting Materials on the Removal of E2.

Different salts like CaCl_2 , MnCl_2 , FeCl_2 , MgCl_2 , and FeCl_3 (1 mg/L) were added to the reactor for investigation of the effect of ions on degradation of E2 at optimum pH 4. Minerals and organic salts can be effective in eliminating target pollutants through oxidation of permanganate [20, 22, 23]. Therefore, the removal efficiency of E2 under the influence of some ions in aqueous media was investigated, and the results are shown in Figure 2. The presence of Mg^{+2} and Fe^{+3} ions had a significant negligible influence on E2 removal $83.9 \pm 0.3\%$ and $76.15 \pm 1\%$, respectively. Adding Ca^{+2} , Mn^{+2} , and Fe^{+2} ions to the solution enhanced the E2 removal rate from $93.7 \pm 0.14\%$ to $93.8 \pm 0.84\%$, $94.8 \pm 0.3\%$, and $95.55 \pm 0.07\%$, respectively. Therefore, in this case, the adsorption of Ca^{+2} , Mn^{+2} , and Fe^{+2} ions, which are positively charged, onto the colloidal MnO_2 surface would mitigate the negative charge of MnO_2 and decrease the electrostatic repulsion between MnO_2 and negatively charged pollutants [24]. Consequently, the reduction of MnO_2 to Mn^{+2} by negatively charged pollutants was accelerated (as illustrated in Figure 2) so that E2 oxidation was enhanced accordingly. On the other hand, competition for active MnO_2 sites between the Mg^{+2} and Fe^{+3} ions with E2 molecules had detrimental effects on E2 removal that led to a significant reduction in oxidation efficiency. These results are similar to study [3]. They used the combined KMnO_4 /ultrasound system and stated that humic acid, reducing agents (SO_3^{2-} and NO_2^-), complexes (EDTA, citrate, and oxalate), HCO_3^- , and phosphate can enhance the oxidation of steroid estrogens. Common ions in natural waters such as Mn^{+2} , Fe^{+2} , and Ca^{+2} can slightly enhance the

TABLE 2: Degradation kinetic parameters of E2 under optimum pH.

Steroid estrogen	pH	Reaction order	Kinetic equation	Reaction rate constant (K)	R^2	Half-life (min)
E2	4	Zero	$y = -0.0061x + 0.6251$	0.0061 (mg.L/min)	0.60	82
		First	$y = 0.022x + 0.5838$	0.022 (1/min)	0.84	31.5
		Second	$y = 0.135x + 1.2172$	0.135 (L/mg.min)	0.93	4

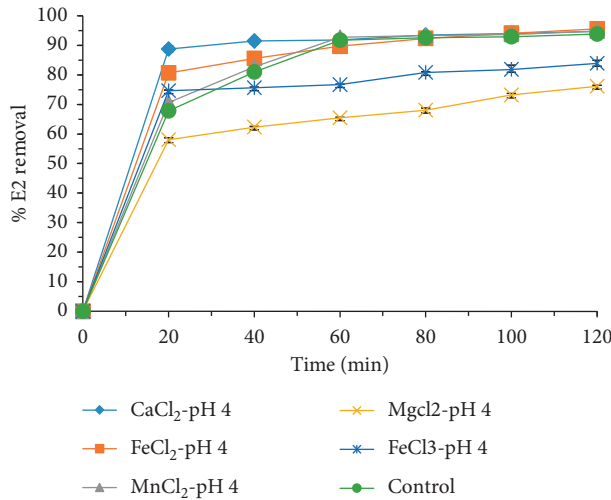


FIGURE 2: Removal percentage of E2 in the presence of coexisting materials for optimum pH.

removal of E1. However, Al^{3+} , Fe^{3+} , and Mg^{2+} reduce estrogen during the oxidation process of permanganate.

Compatible with our findings, phosphate buffer, pyrophosphate, EDTA, and humic acid, as well as real water background matrix, significantly increased BPA oxidation with manganese (VII) over a wide range of pH. Sun et al. found that the presence of Ca^{2+} not only accelerated the rate of methyl blue decomposition but also improved the removal efficiencies of methyl blue by $\text{MnO}_2/\text{HSO}_3^-$ [25]. Shao et al. studied the removal of E1 by permanganate in different matrixes and found that the efficiency of removing E1 in natural water was significantly better than in an ultrapure water system [26]. Pétrier et al. observed that carbonate radicals produced from bicarbonate ions in natural waters are desirable for the removal of micropollutants [27].

Table 3 shows that in the presence of Ca^{+2} , Mn^{+2} , Fe^{+2} , Mg^{+2} , and Fe^{+3} , the second-order reaction had a relatively high linearity with high correlation coefficients (R^2) 0.981, 0.941, 0.946, 0.915, and 0.922, respectively. There is a slight correlation coefficient in the first- and second-order kinetic models (R^2). It can be concluded that in the kinetic reaction of the second order, E2 oxidation is the best. The result indicates that the rate of oxidation of E2 in presence of Ca^{+2} , Mn^{+2} , Fe^{+2} , Mg^{+2} , and Fe^{+3} ions is related to the second exponent of the initial concentration of E2, which enhances the concentration of E2 leading to an increase in the rate of oxidation.

3.3. Effect of Polyaluminum Chloride (PAC) on the Removal of E2. Al-based coagulants, especially alum, are used for effective removal of turbidity and organic matter that may lead

to increase in the concentrations of aluminum in treated water [28]. Therefore, due to the presence of aluminum in the water, the effect of Al^{3+} ions on the E2 removal process has been investigated, and the results are shown in Figure 3. The elimination of E2 reduced significantly to 84.15 ± 0.07 , in the presence of 5 mg/L of PAC ($p < 0.05$). Al^{3+} might play a similar role to Fe^{+3} , which competes with E2 to react with permanganate. Deng et al. indicated that coagulation of PAC has an inhibitory effect on the degradation because the excess of Al^{3+} ions produced in coagulation by the hydrolysis of PAC ($\text{Al}_2(\text{OH})_n\text{C}_{16-n}$) enhanced by ultrasound had an adverse effect on the oxidation by the combined $\text{KMnO}_4/\text{ultrasound}$ process, which is consistent with our results [3].

Table 4 shows that in presence of PAC, the second-order reaction had a relatively high linearity with a high correlation coefficient $R^2 = 0.854$. Zero- and first-order kinetic models had low correlation coefficients (R^2). It can be concluded that the second-order kinetic reaction was best applicable in describing oxidation of E2. The result indicates that the rate of oxidation of E2 in presence of PAC is related to the second exponent of the initial concentration of E2, which increases the concentration of E2 leading to an increase in the rate of oxidation.

3.4. Effect of HA, FA, and Their Simultaneous Application on the Removal of E2. Soluble organic matter (DOM) such as humic acid (HA) and folic acid (FA) mainly contains soluble humic matter (DHS) [29]. In the aquatic systems, dissolved organic carbon (DOC) substances have high activity and have effect on ecosystem function by numerous biochemical reactions with hydrous metal oxides and metal ions [30]. Due to the high activity of DOM in water, the effect of HA, FA, and their combination on the E2 removal system was tested, and the results are shown in Figure 4. Adding HA, FA, and their simultaneous application to the solution increased the E2 removal rate from $93.8 \pm 0.42\%$ to $99.87 \pm 0.01\%$, $99.9 \pm 0.06\%$, and $99.93 \pm 0.014\%$, respectively. The effect of HA on the oxidation of phenols by permanganate is attributed primarily to the reduction properties of HA, which increases MnO_2 production under acidic conditions, and secondly to the complex ability of HA, which can stabilize the formed MnO_2 and prevent it from precipitating [31]. Materials having a component (e.g., carbonaceous material) of high adsorption property and a component of high photocatalytic activity can act as a composite for organic pollutants. In addition, the efficient transport charge of the carrier must also occur from electron excitation of semiconductor components [32]. The removal of hormones is increased to approximately 95% by adding humic acid (10 mg L^{-1}) to the solution [33]. However, Haudong et al. demonstrated that by adding humic acid to

TABLE 3: Degradation kinetic parameters of E2 in presence of coexisting materials for optimum pH.

Steroid estrogen	Salt	pH	Reaction order	Kinetic equation	Reaction rate constant (K)	R^2	Half-life (min)
E2	CaCl ₂	4	Zero	$y = -0.006x + 0.5982$	0.006 (mg.L/min)	0.56	83
			First	$y = 0.0235x + 0.6459$	0.0235 (1/min)	0.86	29
			Second	$y = 0.1773x + 0.5377$	0.1773 (L/mg.min)	0.98	6
	MnCl ₂	4	Zero	$y = -0.0061x + 0.6095$	0.0061 (mg.L/min)	0.58	82
			First	$y = 0.023x + 0.6294$	0.023 (1/min)	0.84	30
			Second	$y = 0.1581x + 1.0959$	0.1581 (L/mg.min)	0.94	6
	FeCl ₂	4	Zero	$y = -0.0057x + 0.5774$	0.0057 (mg.L/min)	0.52	88
			First	$y = 0.0218x + 0.7036$	0.0218 (1/min)	0.85	32
			Second	$y = 0.1646x + 0.4241$	0.1646 (L/mg.min)	0.95	6
	MgCl ₂	4	Zero	$y = -0.0047x + 0.7072$	0.0047 (mg.L/min)	0.61	106
			First	$y = 0.0096x + 0.3972$	0.0096 (1/min)	0.77	72
			Second	$y = 0.0228x + 1.4903$	0.0228 (L/mg.min)	0.92	44
	FeCl ₃	4	Zero	$y = -0.0052x + 0.6498$	0.0052 (mg.L/min)	0.56	96
			First	$y = 0.0126x + 0.5436$	0.0126 (1/min)	0.75	55
			Second	$y = 0.0395x + 1.7977$	0.0395	0.92	25

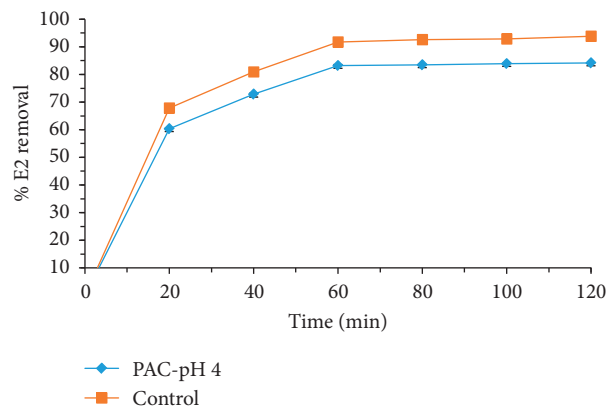


FIGURE 3: Removal percentage of E2 in the presence of PAC for optimum pH.

TABLE 4: Degradation kinetic parameters of E2 in presence of PAC for optimum pH.

Steroid estrogen	Salt	pH	Reaction order	Kinetic equation	Reaction rate constant (K)	R^2	Half-life (min)
E2	PAC	4	Zero	$y = -0.0055x + 0.6638$	0.0055 (mg.L/min)	0.6	91
			First	$y = 0.014x + 0.5162$	0.014 (1/min)	0.76	49.5
			Second	$y = 0.0459x + 1.7828$	0.0459 (L/mg.min)	0.85	22

the solution, the removal of petroleum hydrocarbons was reduced [34]. Yan and Schwartz observed an increase in E2 removal in the presence of HA at all pH values [19]. The results demonstrated that in the presence of HA, the oxidizing power of MnO₂ and Mn (II) adsorption onto the MnO₂ surface was the two competing yet dominant mechanisms in determining the extent of E2 removal. Zhang et al. observed that as the concentration of humic acid increased, the concentration of E1 and E2 decreased, which means an increase in degradation rate constant [23]. This positive effect of humic acid on the optical decomposition of E1 and E2 has been attributed to the sensitization effect of humic acid. These studies confirm our results.

Table 5 shows that in presence of HA, FA, and their simultaneous application, the first-order reaction had a relatively high linearity with high correlation coefficients

(R^2) 0.97, 0.968, and 0.967. Zero- and second-order kinetic models had low correlation coefficients (R^2). It can be concluded that the first-order kinetic reaction was best applicable in describing oxidation of E2. The result indicates that the rate of oxidation of E2 in presence of HA, FA, and their simultaneous application is related to the initial concentration of E2, which increases the concentration of E2 leading to an increase in the rate of oxidation.

3.5. *Determining Mineralization of E2 by UV/KMnO₄ via COD Measurement.* Steroids are present in the environment with high hormonal activity and low concentration and exert their effects at low concentration (ng/L) [3]. Therefore, complete degradation and loss of their hormonal activity are important. The level of degradation of

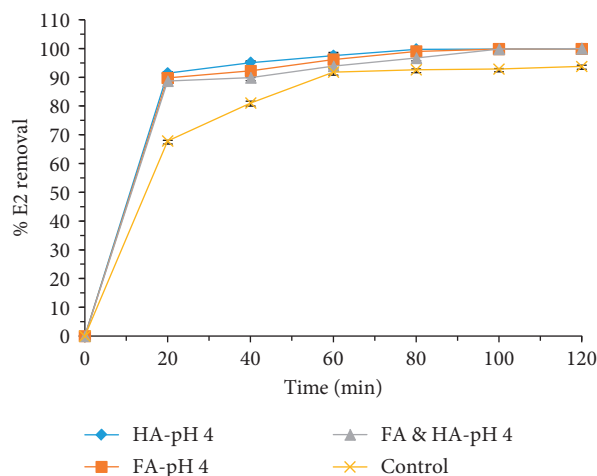


FIGURE 4: Removal percentage of E2 in the presence of HA, FA, and their combination for optimum pH.

TABLE 5: Degradation kinetic parameters of E2 in presence of HA for acidic and neutral pH.

Steroid estrogen	Organic acid	pH	Reaction order	Kinetic equation	Reaction rate constant (K)	R^2	Half-life (min)		
E2	HA	4	Zero	$y = -0.0057x + 0.5104$	0.0057 (mg.L/min)	0.45	88		
			First	$y = 0.0529x + 0.7484$	0.0529 (1/min)	0.95	13		
			Second	$y = 5.9484x - 139.65$	5.9484 (L/mg.min)	0.79	0.2		
			Zero	$y = -0.0062x + 0.6543$	0.0062 (mg.L/min)	0.66	81		
			First	$y = 0.0245x + 0.3082$	0.0245 (1/min)	0.93	28		
			Second	$y = 0.2105x - 2.9462$	0.2105 (L/mg.min)	0.66	5		
	FA	4	Zero	$y = -0.0059x + 0.5396$	0.0059 (mg.L/min)	0.49	85		
			First	$y = 0.055x + 0.1377$	0.055 (1/min)	0.92	13		
			Second	$y = 9.276x - 278.06$	9.276 (L/mg.min)	0.56	0.1		
			HA & FA	4	First	$y = 0.055x + 0.1377$	0.055 (1/min)	0.92	13
					Second	$y = 9.276x - 278.06$	9.276 (L/mg.min)	0.56	0.1
					Zero	$y = -0.0059x + 0.5396$	0.0059 (mg.L/min)	0.49	85

steroid hormones by the UV/KMnO₄ process (indicated by COD removal) was assessed by measuring primary and secondary COD. Removal of COD for E2 after 120 minutes of contact time at optimum pH ($86 \pm 4.2\%$) indicated the mineralization of these compounds at acceptable levels.

4. Conclusion

This study demonstrated that the KMnO₄/UV system is effective in the removal of E2 in the aquatic solution. The results of this study are applicable for the environment, aquaculture industry, industrial and municipal wastewater treatment, and water treatment plants because these contaminant and other estrogenic compounds are found in human and animal disposal waste and have adverse effects. The KMnO₄/UV process in acidic pH can remove E2 from an aqueous system more than that in natural or basic pH condition. The removal rates of E2 were accelerated in the presence of Ca⁺², Mn⁺², and Fe⁺² ions while Mg⁺² and Fe⁺³ ions can decline significantly the efficiency rate. However, it should be taken into consideration that Al³⁺ ions generated from coagulation significantly harm oxidation. HA, FA, and their combination can increase degradation rates of E2 as compared to control without them. In addition, with regards to coexisting steroid estrogens (SEs) in water, it is not

enough to focus on the degradation rate or removal efficiencies; more “sophisticated” toxicity tests, such as YES (yeast estrogen screen), and estrogenicity tests are needed to demonstrate the efficiency of the process. Further studies would benefit from testing higher doses of KMnO₄ to conclusively determine the effect of KMnO₄ addition, as well as the degradation rate in the other endocrine-disrupting chemicals tested by this technique.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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