

HYDROCARBONS IN CRUDE OIL POLLUTED SOIL: REMOVAL USING ACTIVATED PERCARBONATE AND PERSULPHATE

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ABSTRACT

A comparative study of the effectiveness of alkaline activated persulfate and Fe^{2+} activated percarbonate on total petroleum hydrocarbon (TPH) and benzene, toluene, ethylbenzene and xylene (BTEX) was conducted by comparing the concentration of the contaminants before and after treatment with the oxidants. The concentration of the hydrocarbons were analyzed by gas chromatography (GC-FID). The rate of degradation of TPH by Alkaline activated persulphate was 65.07% while that of percarbonate activated by Fe^{2+} is 65.89%. Similarly, alkaline activated persulphate produced a BTEX degradation of 99.88% while Fe^{2+} activated percarbonate produced a degradation rate of 98.23%. The results show that Fe^{2+} activated percarbonate is very efficient in degrading TPH and BTEX and the similarity recorded in rate of degradation by the two oxidants could possibly indicate the similar degradation mechanism.

Key words: Contaminants, crude oil, hydrocarbons, percarbonate, persulphate.

INTRODUCTION

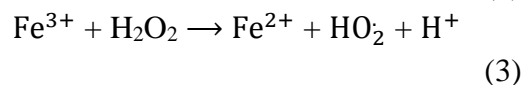
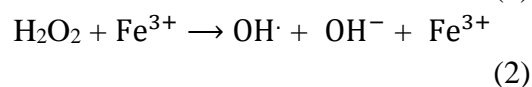
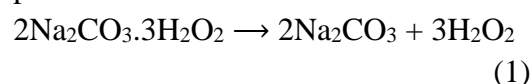
Contamination of soils by anthropogenic contaminants has become a widespread and serious problem threatening the lithosphere and aquifers throughout the globe. These anthropogenic contaminants endanger our environment and cause a severe harmful effect on both plants and animals. The most common contaminants found in our environment are petroleum hydrocarbons (PHCs), polynuclear aromatic hydrocarbons (PAHs), saturated and unsaturated chlorinated solvents, coal tar, heavy metals and pesticides (Lars, 2011). Among these contaminants, the one that poses a serious threat to Niger Delta region in Nigeria is petroleum hydrocarbon from

crude oil spillage. As a result of risks posed by these xenobiotics, there is an urgent need for remediation. *In situ* chemical oxidation (ISCO) has proven to be very effective in removing hydrocarbons from contaminated soil (Ferrarese *et.al*, 2008; Siegrist *et.al*, 2011) and also has been applied under various hydrogeological and soil conditions. *In situ* oxidation involves using strong oxidants to oxidize compounds of concern completely or to a permissible limit and this process may include addition of oxygen, removal of hydrogen or removal of electrons.

This research is focused on two oxidants that contain oxygen – oxygen single bond (peroxy group); percarbonate and

persulfate. This oxygen-oxygen bond splits easily to generate reactive species. Both oxidants can transform wide range of contaminants under various environmental conditions (Siegrist *et al.*, 2011). Sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$) has been researched extensively both in bench and field-scale in ISCO while the use of sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$) has started to get the attention of researchers on its applicability in ISCO. Persulphate can be activated by heat, alkaline solution, hydrogen peroxide, transition metals, chelated-iron, heat to powerful free hydroxyl radicals (OH^{\bullet}) $E_0 = 2.4\text{V}$ or free sulfate radical $\text{SO}_4^{\bullet-}$ ($E_0 = 2.8\text{V}$) (Peyton, 1993, Liang *et al.*, 2007) and other highly oxidative species like ($\text{O}_2^{\bullet-}$, H_2O_2 , HO_2^{\bullet} , H_2SO_5) so as to enhance the oxidation strength, range of applicability and rate of oxidation of organic compounds (Tsai *et al.*, 2008, Block *et al.*, 2004; Sra *et al.*, 2010). The activation method to be selected depends on its effect on the oxidation of organic compound of concern, the ease of its applicability to the subsurface, and how it continually affect the persulphate-activator in the mist of aquifer materials (Block *et al.*, 2004). The method of activation affects the rate of oxidation by persulphate dissociation of sodium percarbonate in water generates sodium trioxocarbonate (IV) and hydrogen peroxide. The hydrogen peroxide product offers similar benefit as the liquid one in that its activation generates hydroxyl radical follows the same mechanism with Fenton chemistry as shown in the Equation (1 – 3) below. Some advantages that catalyzed sodium percarbonate have are: high oxidation potential ($E_0 = 1.78\text{ V vs. SHE}$), high solubility in water, formation of hydroxyl

radicals (OH^{\bullet}) ($E_0 = 2.70\text{V}$) which results in non-selective degradation of organic contaminants, production of by-products that are environmental friendly, ability to oxidize contaminants over a wide range pH, high compatibility with bioremediation due to production of non-toxic by-products that cannot harm neither microbes nor humans (Xiaori *et al.*, 2015). The problem encountered with the field application of sodium persulphate which is frequent changing of any metallic material used due to the reaction of the metal with H_2SO_4 (a byproduct) is eliminated when sodium percarbonate is used.



In this research, the two oxidants were activated using different methods to examine the effects of transformation and removal of (TPH, PAHs and BTEX) as a result of interaction of the contaminants with the oxidants.

MATERIAL AND METHODS

The crude oil used for the experiment was collected from crude oil spill site at Kegbara Dere in Gokhana Local Government Area in Rivers State Nigeria. The soil samples collected were ground, homogenized, and sieved with 2-mm sieve. Five hundred grams (500 g) of the homogenized soil sample were weighed and put into 1L glass beaker. The glass beaker was contaminated with 50 ml of crude oil. The two glass beakers were stirred for 30 minutes to achieve homogeneity, allowed to stand for 72 hrs

equilibration period. The soil samples were analyzed to establish the initial concentration of TPH, PAH and BTEX. Hundred grams (100 g) of the contaminated soil were weighed into each of the three 500 ml glass beakers labeled A₁, A₂ and A₃.

The pH of A₁ was adjusted to 11 using 3M NaOH followed by addition 250 ml of 1M of sodium persulphate. After the solutions (NaOH and Na₂S₂O₈) have been added together, the test reactor was stirred with stirring rod for 30 minutes to ensure they have complete mixing. The stirring rod was removed to allow completion of reaction. The reactor was kept for 7 days after which the soil samples were analyzed for TPH and BTEX concentrations. 250 ml of 1M solution of sodium percarbonate, Na₂CO₃.1.5H₂O was added to A₂. Each solution was stirred for 30 minutes, stored in the dark for 7 days so as to allow the reaction to come to completion. 250 ml of 1M solution of iron (II) tetraoxosulphate (VI) heptahydrate, FeSO₄.7H₂O was added to A₃ and thoroughly mixed using a stirrer, then 250 ml of 1M of sodium percarbonate, Na₂CO₃.1.5H₂O was added to start the reaction. The pH and temperature of the reaction were left unadjusted at room temperature. All the experiments were carried out in triplicate to minimize errors and the mean values were presented as the data and also used for analyzing the data.

The soil samples were freeze-dried and ten grams (10 g) of the soil sample from each microcosm was blended with 10 g of anhydrous sodium sulphate in an extraction

thimble. One hundred and fifty millilitres (150 ml) of methylene chloride was placed into a round bottom flask containing some clean boiling chips. The extraction thimble was allowed to drain freely throughout the extraction period. The flask was joined to the Soxhlet extractor and the sample extracted for 4-6 hours. The extract was allowed to cool after the extraction process and concentrated in a rotary evaporator at 60 °C to 2 ml. The solvent-exchanged extracts were finally transferred to 3.0 g silica gel chromatographic column, which was topped with 1 cm³ anhydrous sodium sulphate which had been previously conditioned using 20 ml of hexane for sample clean up and fractionation. TPH concentration were analyzed by gas chromatography (GC-FID) (varian CP-3800) under the following conditions: HP-5MS 30 m x 0.25 mm capillary column; hydrogen carrier gas; inlet temperature 300 °C; start temperature 50 °C; programmed to 300 °C at a rate of 20 °C/min for 7 minutes; retained for 21.50 min until complete elution of all species. The initial temperature for the analysis of BTEX was set at 30°C for 1 minute and was later increased to 180°C at the rate of 50°C/min and later to 230°C at the rate of 20°C/min using helium as carrier gas. The concentration of BTEX and TPH in the eluent was measured using liquid-liquid extraction method. The N-hexane extract was directly introduced into a GC-Mass spectrometer (MS) for analysis.

RESULTS**Table 1: Calculated amount and % loss of the TPH components of crude oil contaminated soil before and after application of various oxidants**

Crude Oil Sample	Before remediation (mg/kg)	A₁ after remediation (mg/kg)	A₂ after remediation (mg/kg)	A₃ after remediation (mg/kg)	% loss for A₁	% loss for A₂	% loss for A₃
C8	632.5153	0.1327	8.4745	4.6854	99.979	98.6602	99.2592
C9	664.2255	4.0440	40.3018	29.0749	99.3912	93.9325	95.6227
C10	725.0140	45.2432	84.1068	66.7075	93.7597	88.3993	90.7991
C11	592.1899	26.1678	42.7545	74.5766	95.5812	92.7803	87.4066
C12	651.0208	83.4860	31.1448	97.6158	87.1761	95.216	85.0057
C13	746.0034	190.3249	83.7202	147.4374	74.4874	88.7775	80.2364
C14	564.0500	156.1931	49.9222	148.7771	72.3086	91.1493	73.6234
C15	742.3655	184.2904	101.6025	222.1796	75.1753	86.3137	70.0714
C16	592.5135	289.9539	78.4569	312.4109	51.0638	86.7586	47.2736
C17	388.8354	171.6381	72.0215	210.4921	55.8584	81.4776	45.866
Pr	633.7127	401.4477	148.1037	312.4015	36.6515	76.6292	50.703
C18	359.5486	201.7367	88.2008	176.4968	43.8917	75.469	50.9116
Ph	303.8253	147.0272	67.2163	177.1203	51.608	77.8767	41.7032
C19	242.5259	139.0491	64.8041	144.7183	42.6663	73.2795	40.3287
C20	252.9650	185.5278	97.4656	174.0585	26.6587	61.4707	31.1927
C21	217.6636	135.6165	114.5903	144.3383	37.6945	47.3544	33.6874
C22	168.9680	131.1281	83.3570	120.7814	22.3947	50.667	28.5182
C23	156.4032	109.2664	48.4840	113.7523	30.138	69.0006	27.2698
C24	164.8555	107.2361	28.9000	112.8306	34.9515	82.4695	31.5579
C25	187.2551	112.3315	29.1881	99.7193	40.0115	84.4127	46.7468
C26	170.2189	101.4060	30.1873	97.8774	40.4261	82.2656	42.4991
C27	131.1989	83.6179	38.4097	74.8698	36.2663	70.7241	42.9341
C28	132.4879	98.2715	27.1623	71.7377	25.8261	79.4983	45.8534
C29	170.5552	100.6033	36.3204	96.3578	41.0142	78.7046	43.5035
C30	139.5440	86.7154	32.0056	71.3724	37.858	77.0642	48.8531
C31	232.0745	88.7673	33.2471	60.6302	61.7505	85.674	73.8747
C32	116.2397	76.7543	20.6406	52.0814	33.969	82.2431	55.1948
C33	56.1426	49.0564	29.2527	44.0095	12.6218	47.8957	21.6112
C34	110.3020	47.7626	7.1468	3.8075	56.6983	93.5207	96.5481
C35	6.3271	21.1100	5.0355	24.0457	-233.64	20.4138	-280.04
C36	12.6060	8.9223	6.0476	18.3566	29.2218	52.026	-45.618
C37	11.1266	3.4704	0.0238	0.9574	68.8099	99.7861	91.3954
C38	2.3632	0.4757	0.3883	0.0200	79.8705	83.5689	99.1537
C39	1.8690	0.4966	0.0563	0.1297	73.4296	96.9877	93.0605
C40	0.3553	0.4796	0.0218	0.0600	-34.985	93.8643	83.1129
Total	10279.8691	3589.7507	1628.7617	3506.4883	65.07980	84.15581	65.88976

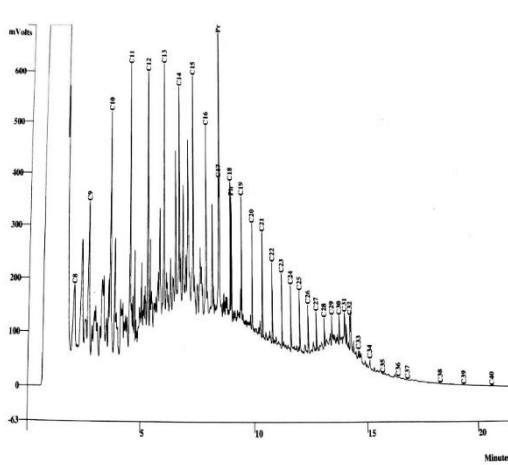


Figure i: Chromatogram showing the distribution of TPH components in crude oil contaminated soil before treatment with various oxidants.

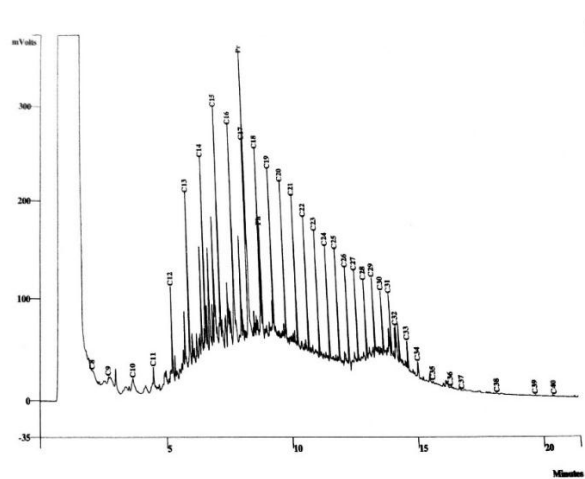


Figure ii: Chromatogram showing TPH components in crude oil contaminated soil after treatment with alkaline activated persulphate (A1).

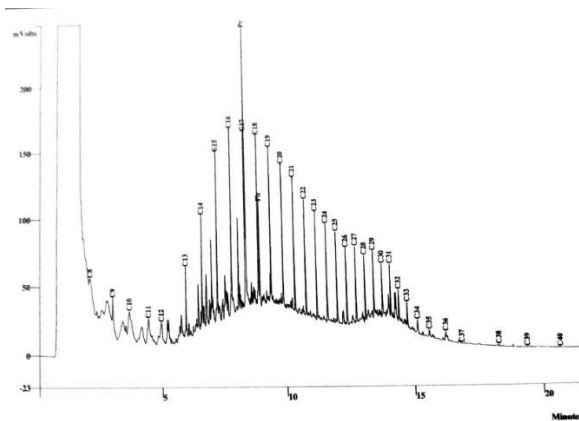


Figure iii: Chromatogram showing TPH components in crude oil contaminated soil after treatment with unactivated percarbonate (A2).

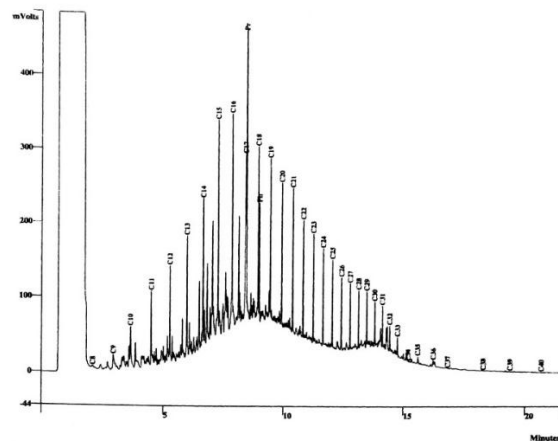


Figure iv: Chromatogram showing TPH components in crude oil contaminated soil after treatment with percarbonate activated with Fe^{2+} (A3).

Table 2: Amount of BTEX components in crude oil contaminated soil before and after remediation.

Sample Crude Oil	Amount (mg/kg) before treatment	A ₁ after treatment	A ₂ after treatment	A ₃ after treatment
Benzene	76.8	-	5.1	14.4
Toluene	222.5	0.5	0.6	1.1
Ethylbenzene	133.2	0.4	2.7	1
p-Xylene	847	0.2	22	4.7
o-Xylene	137	0.5	4.9	1.3
Total	1416.5	1.6	35.3	22.5

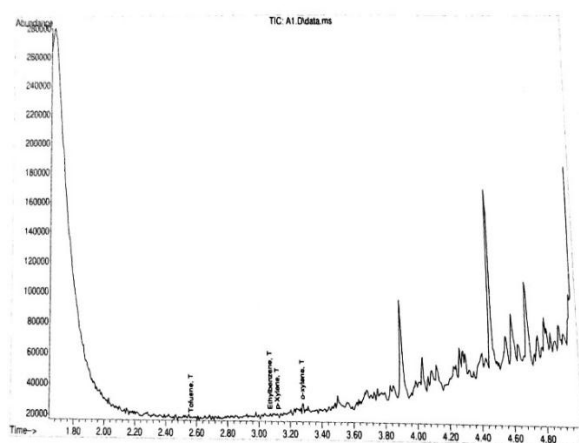


Figure v: Fingerprints of BTEX in crude oil contaminated soil before treatment with various oxidants.

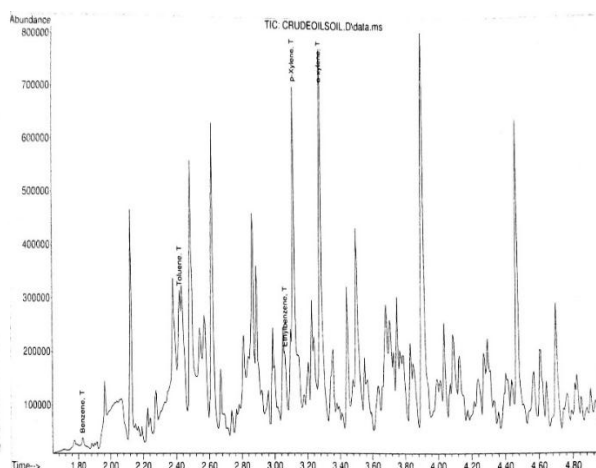


Figure vi: BTEX components of crude oil contaminated soil treated with alkaline activated persulphate (A1)

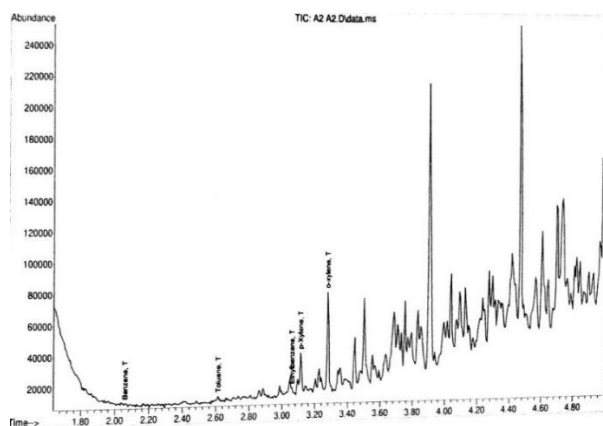


Figure vii: BTEX components of crude oil contaminated soil treated with unactivated percarbonate (A₂).

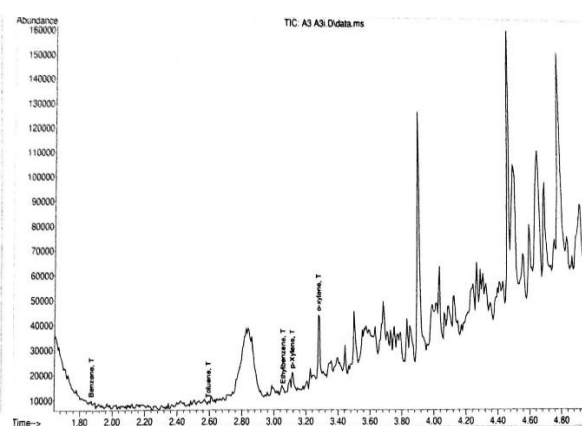


Figure viii: BTEX components of crude oil contaminated soil treated with percarbonate activated with Fe²⁺ (A₃)

DISCUSSION

The chromatogram showing the components of crude oil before treatment is shown in Fig i while the degree of degradation of TPH in crude oil contaminated soil using various oxidants was shown Fig. i - iv. Alkaline activated persulphate (A₁) produced a TPH degradation of 65.07%, unactivated percarbonate (A₂) produced a degradation of 84.16% while percarbonate activated by Fe²⁺ (A₃) produced a degradation rate of 65.89% as shown in Table 1.

Though unactivated percarbonate (A₂) had the highest degradation rate based on the soil sample analysis as seen in Table 1 above, its efficiency is not as that of alkaline activated persulphate and Fe²⁺ activated percarbonate. The solutions in the microcosms at the end of the reaction have different appearances which also reflect the degree of the efficiency of their oxidation. Solution A₁ and A₃ were clear while that of A₂ has black colouration. The clarity of the solution formed on each microcosm after treating it with various oxidants is

lowest in A₂ while the microcosm with the best clear solution was that of A₁. Though A₃ has a higher degradation rate than A₁, the traces of brownish solution of the A₃ after 7 days could be ascribed to the oxidation of green Fe²⁺ to brown Fe³⁺. Dissolution of sodium percarbonate in water produces sodium carbonate and hydrogen peroxide (Equ. 3). The latter being a strong oxidant at a low pH, can oxidize hydrocarbon like TPH into harmless products like carbon (IV) oxide and water or oxygenate the hydrocarbon by OH[•] radical mechanism into its equivalent alkyl hydroperoxide, ROOH as the major primary product (oxygenase activity) which could further decompose, yielding more stable products like ketone, aldehyde and smaller chain alcohols which are water soluble compounds and also a solvent for non-polar compounds like hydrocarbons (Lide, 2016, Georgiy *et al.*, 2004 and María *et al.*, 2005). The decrease in TPH of A₂ could be attributed to volatilization or oxidation of higher molecular mass hydrocarbons into lower molecular mass hydrocarbon and oxygenation of short chain hydrocarbon into ketone, aldehydes and alcohol. The black colouration of the soil and solution above the soil could be as a result of the dissolution of some components of TPH in the soil, ketones and aldehydes formed in the water soluble alcohols. Some metals in the soil like Fe²⁺ could have acted as a catalyst which aid in the decomposition of the hydrogen peroxide and in oxygenation of the TPH. Activation of percarbonate by Fe²⁺ produces OH[•] while alkaline activation of persulphate produces OH[•], SO₄^{•-} and reductant (Watts, 2011). Liang, 2007 showed that, while SO₄^{•-} is the main active specie at pH <7, OH[•] is the main

active specie at pH >10. The mechanism of breakdown of crude oil components in soil by alkaline activated persulfate and percarbonate activated by Fe²⁺ are alike since both degrade by producing hydroxyl radical (OH[•]) which oxidizes the hydrocarbon. This explains the closeness in the average percentage rate of reduction/degradation by alkaline activated persulphate and percarbonate activated by Fe²⁺. There seems to be a little difference in amount of TPH degraded from C₁₈ - C₂₅ as shown in Fig ii - vi. This could be due to the oxidative degradation of long chain hydrocarbon to that of short chain hydrocarbon that fall within that range.

BTEX degradation by different oxidants

In microcosm where no activating agent was added (A₂), the rate of degradation was found to be the lowest. The decrease in BTEX components in A₂ could be attributed to volatilization of BTEX components or due to their dissolution in the resulting solution formed due to oxygenation of TPH components to form a polar covalent compound like alcohol as described above. The percentage of degradation of BTEX by these oxidants is very high when compared with TPH. The efficiency of activated persulphate and percarbonate in destruction of BTEX is clearly shown in Table 2 which shows the concentration of BTEX in crude oil contaminated soil before and after treatment. Fig vi – viii above show a graphical presentation of the effects of these oxidants on the contaminant.

Alkaline activated persulphate (A₁) produced a BTEX degradation of 99.88% in which there was complete removal of benzene. Unactivated percarbonate (A₂) produced a degradation of 97.51% while

percarbonte activated by Fe^{2+} (A_3) produced a degradation rate of 98.41%. It is very interesting to note that there was almost 100% removal of each component of BTEX when treated with alkaline activated persulphate as shown in Table 2 and Figure vi. The Fig vi - viii above shows that both oxidants when activated can efficiently reduce the concentration of BTEX in a crude oil contaminated soil. The oxidants used in this experiments have shown that they can reduce the concentration of the contaminants of concern (TPH and BTEX) but their rate of degradation differs with respect to the contaminant and they were most effective in removing BTEX.

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