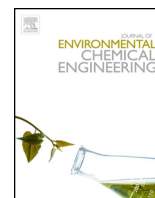




Contents lists available at ScienceDirect

## Journal of Environmental Chemical Engineering

journal homepage: [www.elsevier.com/locate/jece](http://www.elsevier.com/locate/jece)

## Reducing polycyclic aromatic hydrocarbons content in coal tar pitch by potassium permanganate oxidation and solvent extraction

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## ARTICLE INFO

## Article history:

Received 21 April 2015

Accepted 26 May 2015

## Keywords:

Coal tar pitch

Potassium permanganate

Oxidation

Polycyclic aromatic hydrocarbons (PAHs)

## ABSTRACT

This study was conducted to assess the feasibility of using potassium permanganate (KMnO<sub>4</sub>) as an oxidant to reduce 7 carcinogenic polycyclic aromatic hydrocarbons (PAHs) content in two coal tar pitches (CTPs), and to research the oxidation mechanism of KMnO<sub>4</sub>. It had been observed reduction of major PAHs in CTP after KMnO<sub>4</sub> oxidation. The best benzo[a]pyrene equivalency (BaP<sub>eq</sub>) reduction rate of 82% in *n*-hexane soluble in a high temperature CTP (HCTP) was achieved with KMnO<sub>4</sub> concentration of 0.2 M treated for 5 h. Specifically, a higher phenanthrene reduction rate (90%) was obtained by using the Soxhlet extraction with *n*-hexane as solvent on the KMnO<sub>4</sub> oxidized HCTP. The single PAH removal rate roughly increases with increasing rings number of PAH, following the order of phenanthrene < fluoranthene < pyrene < benzo[a]pyrene < benzo(b)fluoranthene < indeno [1,2,3-*ed*]pyrene < benzo[g,h,i]perylene under the same conditions. By using gel penetration chromatography (GPC) and gas chromatography–mass spectrometry (GC–MS), electrophilic substitution reaction was speculated as the oxidation mechanism of CTP by KMnO<sub>4</sub>.

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## Introduction

Coal tar pitch (CTP), the remnant of distillation process from coal tar, contains about 200 polycyclic aromatic hydrocarbons (PAHs) [1], PAHs are aromatic compounds containing from two to six benzene rings, many of them are highly toxic, carcinogenic, teratogenic and thermally stable [2–4]. 16 PAHs (Table 1) in CTP have been identified as priority carcinogenic compounds by the US Environmental Protection Agency (US EPA) [5,6]. CTP is commonly found in many industrial areas like former manufactured gas plants, steel making plants, mesocarbon/microbeads electrodes for the metallurgy and material of pavement industry [7–10]. Coal tar have accumulated over decades in soils of the related fields, it can penetrate the entire 4–5 m thickness of soil, refractory to biodegradation, and persistent in soil and water [11–14], therefore, in recent years, coal tar or the related product is considered the fundamental PAHs source among all the known sources [15,16], especially in places like coal-tar-based sealcoat, it has been

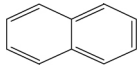
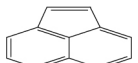
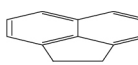
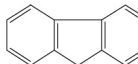
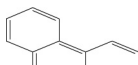
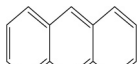
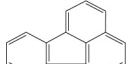
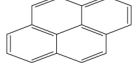
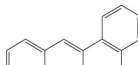
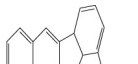
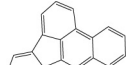
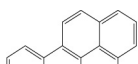
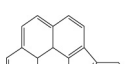
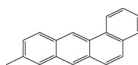
identified that CTP contributes to a major source of PAHs, PAHs concentration in dust is about 1000 times higher than asphalt-based sealcoat pavement [17]. PAHs in particles can be easily transported by wind and rainwater to nearby soil sediments, water and air, lead to increased cancer risk for human beings [18–20]. Therefore, CTP is thought as a potential pollutant for its toxic PAHs components [21], and considerable restriction of the application areas for CTP is currently observed.

For those reasons, to prepare less toxic CTP is a matter of extreme importance to environment and human health. Several researches have reported removing carcinogenic PAHs from CTP [22–27]. Boyd et al., Dix and Marnett explained the transformation mechanism of benzo[a]pyrene (BaP) which is the most common and most dangerous PAHs carcinogens to human beings and investigated the carcinogenic mechanism. They pointed out that BaP would be converted into harmless as some functional groups substitute the active position of BaP. This mechanism can be summarized according to the reaction sequence in Fig. 1 [28,29]. Some researchers used polymers at high temperature for a long time to reduce the carcinogenic PAHs content in CTP, such as unsaturated polyester resin (UPR), polyethylene glycol (PEG), 1,4-benzenedimethanol (PXG), divinylbenzene (DVB) and so on

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**Table 1**  
Relative potency factor (RPF) of each PAH and property according to the US EPA OPPTS.

PAH species	Chemical structure	Chemical formula	Number of aromatic rings	Molecular weight (g/mol)	Boiling point (°C)	RPF	Abbreviation
Naphthalene		C <sub>10</sub> H <sub>8</sub>	2	128.16	217.9	0.000	NAP
Acenaphthylene		C <sub>12</sub> H <sub>8</sub>	3	152.2	275	–	ACY
Acenaphthene		C <sub>12</sub> H <sub>10</sub>	3	154.21	279	–	ACP
Fluorene		C <sub>13</sub> H <sub>8</sub>	3	166.22	298	0.000	FLR
Phenanthrene		C <sub>14</sub> H <sub>10</sub>	3	178.23	340	0.000	PHE
Anthracene		C <sub>14</sub> H <sub>10</sub>	3	178.23	345	0.000	ANT
Fluoranthene		C <sub>16</sub> H <sub>10</sub>	4	202.26	367	0.034	FLT
Pyrene		C <sub>16</sub> H <sub>10</sub>	4	202.26	393.5	0.000	PYR
Benzo(a)anthracene		C <sub>18</sub> H <sub>12</sub>	4	228.29	438	0.033	BaA
Benzo(k)fluoranthene		C <sub>20</sub> H <sub>12</sub>	5	252.3	481	0.010	BbF
Benzo(b)fluoranthene		C <sub>20</sub> H <sub>12</sub>	5	252.3	481	0.100	BbF
Benzo[a]pyrene		C <sub>20</sub> H <sub>12</sub>	5	252.3	500	1.000	BaP
Indeno[1,2,3-ed]pyrene		C <sub>22</sub> H <sub>12</sub>	6	276	–	0.100	IcP
Dibenzo[a,h]anthracene		C <sub>22</sub> H <sub>14</sub>	5	278.35	–	1.400	DhA

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