NITROGEN-DOPED BIOCHAR AS PEROXYMONOSULFATE ACTIVATOR FOR ACID ORANGE 7 REMOVAL

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by

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LIST OF SYMBOLS

I_D/I_G	Ratio of intensity of D and G bands
χ	Electronegativity
$SO_4^{\cdot-}$	Sulfate radical
$^{\cdot}OH$	Hydroxyl radical
$^1O_2$	Singlet oxygen
$O_2^{\cdot-}$	Superoxide ion radical
k_{app}	Pseudo first order rate constant

LIST OF ABBREVIATIONS

AC	Activated Carbon
AO7	Acid orange 7
AOPs	Advanced oxidation processes
BPA	Bisphenol A
CNTs	Carbon nanotubes
DFT	Density functional theory
DOC	Dissolved organic carbon
EDX	Electron dispersive spectroscopy
EtOH	Ethanol
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared
GAC	Granular activated carbon
GO	Graphene oxide
DOM	Dissolved organic matter
NB	Nitrobenzene
NBCs	N-doped biochar catalysts
NH_3	Ammonia
OMC	Ordered mesoporous carbon
PAC	Powdered activated carbon
PDS	Peroxydisulfate
PMS	Peroxymonosulfate
PS	Persulfate
rGO	Reduced graphene oxide
ROS	Reactive oxygen species
SSA	Specific surface area

SWCNT	Single- walled carbon nanotube
TGA	Thermogravimetric analysis
TOC	Total organic carbon
UV-Vis	Ultraviolet- visible
XPS	X-ray photoelectron spectroscopy
XRD	X- ray diffraction

BIORANG TERDOP NITROGEN SEBAGAI PENGAKTIF PEROKSIMONOSIDA UNTUK PENYINGKIRAN OREN ASID 7

ABSTRAK

Proses pengoksidaan lanjutan (AOP) berasaskan pengaktifan peroksimonosida (PMS) bagi penyingkiran bahan organik telah menjadi subjek yang popular dalam bidang kimia persekitaran. Pada bahagian pertama kajian (Bab 4), bioarang terdop oksigen disediakan dengan menggunakan habuk papan melalui proses termal dan keadaan optimum ditentukan. Produk bioarang yang terhasil dinamakan sebagai C800. Sifat kimia dan fizikal C800 dicirikan dan didapati C800 dapat digunakan sebagai pemangkin berprestasi tinggi atas faktor permukaan spesifiknya yang tinggi (993 m^2 g^{-1}) dan kewujudan kumpulan ketonik yang aktif. Ujian kecekapan menunjukkan bahawa C800 berkesan untuk menyingkirkan oren asid 7 (AO7) dan tren penguraian AO7 dipengaruhi secara signifikan oleh dos PMS dan muatan pemangkin. Ujian kebolehgunaan semula C800 menunjukkan penurunan kemampuannya sebagai pemangkin setelah digunakan selama beberapa kitaran akibat pengoksidaan kanibalistik di atas permukaan C800. Walaupun begitu, penyingkiran DOC sebanyak 70% menunjukkan tahap mineralisasi yang tinggi serta pembukaan cincin bahan perantaraan aromatik AO7 dapat dicapai. Mekanisme reaksi didapati dipengaruhi oleh laluan radikal dan laluan bukan radikal. Pada bahagian kedua kajian (Bab 5), pemangkin bioarang terdop nitrogen dari habuk papan dan urea disediakan melalui kaedah sintesis satu periuk untuk pengaktifan PMS. Didapati bahawa nisbah antara urea dan habuk papan mempunyai peranan penting dalam mengawal komposisi spesies N dalam bioarang terdop nitrogen. Nisbah urea kepada habuk papan dibezakan dari 0:1 hingga 100:1 dan ciri kimia dan fizikal bioarang terdop nitrogen yang terhasil dikaji. Gabungan ciri kimia (at.% grafitik N tertinggi) dan ciri fizikal (luas permukaan spesifik tertinggi) pemangkin yang mempunyai nisbah w/w urea:habuk papan 100:1 (NC800-20) menjadikan NC800-20 sebagai pemangkin yang terbaik untuk proses pengaktifan PMS bagi penyingkiran bahan organik. Proses pengaktifan PMS didapati dipengaruhi oleh dos PMS, muatan pemangkin, dan pH. NC800-20 mempunyai aktiviti pemangkin terbaik untuk menyingkirkan pelbagai bahan pencemar organik dalam keadaan optimum. Kebolehgunaan semula NC800-20 disiasat dan didapati bahawa prestasi NC800-20 menurun tetapi proses kalsinasi sederhana pada 500˚C dapat memulihkan kecekapan pemangkin sepenuhnya. Penyelidikan menyeluruh mengenai pemangkin terpakai telah dibuat dan mekanisme pengaktifan PMS ditentukan. Didapati bahawa laluan bukan radikal adalah mekanisme utama untuk pengaktifan PMS. Secara keseluruhan, kajian pertama menunjukkan bioarang terdop oksigen yang disediakan daripada sisa buangan melalui kaedah mudah dapat bertindak sebagai pengaktif PMS yang efektif. Kajian kedua memberi pengetahuan baharu mengenai penyediaan bioarang terdop nitrogen dengan sifat kimia dan fizikal daripada sisa buangan untuk penyingkiran pencemar organik melalui pengaktifan PMS.

NITROGEN-DOPED BIOCHAR AS PEROXYMONOSULFATE ACTIVATOR FOR ACID ORANGE 7 REMOVAL

ABSTRACT

Advanced oxidation processes (AOP) as a method for organic pollutant removal via peroxymonosulfate (PMS) activation has recently become a popular subject in the field of environmental chemistry especially in the organic degradation process. In the first part of the study (Chapter 4), the preparation of oxygen functionalized biochar was optimized by using a facile one-pot thermal treatment of sawdust. The resultant biochar product was denoted as C800. The intrinsic and extrinsic properties of C800 was characterized and found to be a promising catalyst due to its high specific surface are (993 m^2g^{-1}) and ketonic group's active sites. The performance test showed that C800 is effective to degrade acid orange 7 (AO7) and the trend of degradation reaction was significantly influenced by PMS dosage and catalyst loading. C800 reusability test showed the decrease of its capability after used for several cycles due to its cannibalistic oxidation of C800 surface. Nonetheless, 70 % of DOC removal that indicate a high mineralization extent as well as the opening ring of aromatic AO7 intermediates was accomplished. The reaction mechanism was found to be influenced by radical and nonradical pathway. In the second part of study (Chapter 5), N-doped biochar catalyst from sawdust and urea as parent materials was successfully produced via a facile and scalable one-pot synthesis method for PMS activation. It was found that the ratio between urea and sawdust had an important role in tuning the N species composition in the N-doped biochar. A different ratio urea: sawdust was applied from 0:1 to 100:1 and the intrinsic and extrinsic characteristic were studied. A combination of intrinsic (highest at.% graphitic N) and extrinsic (high specific surface area) characteristics of the catalyst that has w/w ratio urea: sawdust of 100: 1 (NC800-20) showed excellent performance in PMS activation process of organic removal reaction. PMS activation was found to be affected by PMS dosage, catalyst loading, and pH. NC800-20 performs good catalytic activity to remove various organics pollutant under optimum condition. The reusability of NC800-20 was investigated over consecutive cycles, and it was found that the performance of NC800-20 was declined but simple calcinations process at 500˚C can recover the catalyst capability completely. A thorough investigation on the used catalyst was applied and the mechanism of PMS activation was revealed. It was found that nonradical pathway was the predominant mechanism for PMS activation. Overall, the first study shows the oxygen-functionalized biochar that obtained from biowaste through facile method is the promising catalyst as PMS activator and the second study provides insights into N-doped biochar preparation with favourable intrinsic and extrinsic properties from biowaste for sustainable pollutant removal via PMS activation.

CHAPTER 1

INTRODUCTION

1.1 Background

The deleterious impact of anthropogenic organics on the environment has created a serious problem to all the inhabitants [1]. For instance, high concentration of recalcitrant organics could be produced mainly from various industrial activities such as paper fabrication, tanning, and textile-dying manufacture [2]. In particular, textile industry effluent containing organic dyes with complicated structure are difficult to treat because of their recalcitrant nature [3–4]. Typically, the most widely used dye is the azo dyes (~70% of the total commercial dye usage) which contain aromatic groups attached to one or more azo (–N=N–) moiety [5–8].

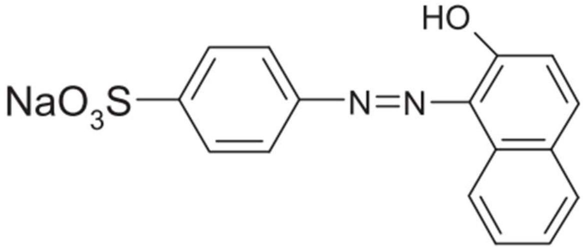

Figure 1.1: Molecular structure of acid orange 7.

Many researchers investigated the process of dye decolorization because of this huge impact on health and the environment. Besides direct implication on aesthetic problem and hampering the depth of light infiltration into the water [1–7], the textile dyes also are very harmful and carcinogenic carrier to human [8]. The presence of dyes in the environment needs to be addressed properly [9–17]. Currently, the treatment processes for removing harmful textile dyes from aquatic environments are either not guarantee for a complete mineralization or complicated [18–20]. Thus, a proper degradation process of these dyes in order to produce the safe, efficient, and environmentally friendly is needed.

Several researchers proposed the use of membrane technology and adsorption as potential treatment strategies [7, 21, 22]. However, these strategies have some disadvantages such as incomplete removal, generate unwanted secondary product and high treatment cost. To date, advanced oxidation processes (AOPs) as a method for organic pollutant removal is gaining a lot of attention. The removal process using AOP technique via peroxymonosulfate (PMS) activation has recently become a popular subject in the field of environmental chemistry especially in the organic degradation process [23–30]. PMS has some more advantages over other commonly used oxidants (i.e. H_2O_2) such as being environmentally friendly, inexpensive and can achieve total mineralization of pollutants. PMS is an oxidant that can be obtained commercially as Oxone®. The Oxone® is a triple salt consisting of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ and it is stable, has high solubility in water, easy to handle and store. The standard electrode potential for PMS is +1.81 V with the HSO_4^- ion is generated in a half reaction (1.1) [31].

$$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O \tag{1.1}$$

PMS can be activated by thermal, alkaline, radiation and catalyst [32]. However, from the methods mentioned above, the most cost-effective method is catalytic PMS activation due to no energy requirement, high removal efficiency and capable of achieving complete mineralization in pollutant degradation reaction. One of the most important parts in the catalytic PMS activation system is the catalyst. In particular, the heterogeneous catalyst is widely use due to its efficiency characteristic and environmentally friendly [34–35]. The catalytic PMS activation can be achieved via radical or nonradical pathways. Radical pathway which generated the reactive species $SO_4^{\cdot-}$ and $^{\cdot}OH$ from peroxide bond fragment. On the other hand, the nonradical pathways rely on interactions between PMS and the target molecules on the catalyst surface to produce either surface activated complex, surface bound radicals or singlet oxygen [25, 33]. There are two types of heterogeneous catalyst that widely used and investigated namely metal- and carbon-based catalyst. Even though the metal-based catalyst is effective, the leaching problem of this catalyst is a big issue. Hence, the using of carbon-based catalyst such as graphene, carbon nanotubes, nanodiamonds, biochar and porous carbon become the better alternative to avoid leaching issue from metal based catalyst [36].

1.2 Knowledge gaps and research motivation

The application of AOPs technologies such as persulfate-based oxidation, Fenton, electrochemical, ozonation, and photochemical oxidation has been widely used in the environmental decontamination. From all mentioned above, persulfate-based oxidation involving peroxydisulfate (PDS) and PMS activation for aqueous organic pollutant degradation is gaining a lot of attention due to its versatility and easy to operate [37–39].

Transition metal ions, metal oxide, and carbonaceous materials can be applied to activate PMS [40]. Previous studies show the using of heterogeneous cobalt as the effective catalyst in the PMS activation process [41, 42]. However, the disadvantage of cobalt catalyst related to the leaching problem which leads to the toxic and carcinogenic agent was discovered [43, 44]. This was the main reason for researchers to shift their focus on another metal catalyst such as iron-, manganese-, and copper-based catalysts. Nonetheless, the leaching problem is still an issue for these metal catalysts [45]. Hence, an alternative to remove this problem is needed.

Most carbon-based catalysts including graphene, carbon nanotube and nano diamonds require expensive precursor. To avoid using expensive precursor, this research is focusing on preparing inexpensive biochar-based catalyst by using a low-cost saw dust as biowaste precursor. The improvement of this catalyst was also investigated by using *in situ* activation/heteroatom doping as a synthesis to endow the catalyst with favorable active sites.

1.3 Objectives and scope of study

The main objective of this research is prepared, characterize, and investigate the performance of heteroatom-doped biochar for organic pollutant removal. The more specific objectives are as follows:

1. To optimize the preparation of oxygen- and nitrogen-functionalized biochar using a facile one-pot thermal treatment of sawdust.

2. To characterize the chemical and physical properties of the as-prepared oxygen- and nitrogen-functionalized biochar.
3. To investigate the performance of oxygen- and nitrogen-functionalized biochar as PMS activator for Acid Orange 7 (AO7) degradation.
4. To determine the PMS activation mechanism by the oxygen- and nitrogen-functionalized biochar during AO7 degradation.

1.4 Organization of thesis

This thesis consists of 6 chapters comprising of (i) Introduction, (ii) Literature Review, (iii) Materials and Methods, (iv) Results and Discussions (two chapters), and (v) Conclusions and Recommendation for Future Research.

Chapter 1: Introduction

This chapter presents an overview of water pollution and possible treatment strategies, particularly AOPs. The current knowledge gap and research motivation of this thesis are also discussed. Thereafter, the research objectives and thesis organizations are outlined.

Chapter 2: Literature Review

This chapter outlines the literature review of carbon-based catalysts covering the types of carbon-based catalysts including activated carbon, graphene, carbon nanotubes, ordered mesoporous carbon, nanodiamonds, and biochar. The performance improvement of the carbon-based catalyst is also reviewed. Lastly, this chapter also discussed the possible mechanisms of PMS activation by carbon-based catalysts.

Chapter 3: Materials and Research methodology

This chapter describes the materials and the method that applied in both of study. Furthermore, this chapter consist of the synthesis process of the research, characterizations, and catalytic performance study.

Chapter 4: Oxygen-functionalized biochar as PMS activator for AO7 removal

This chapter describes the facile synthesis of oxygen functionalized biochar-based catalyst using sawdust. The as-prepared biochar was extensively characterized to investigate their physicochemical properties. Finally, the performance of the biochar was evaluated as PMS activator to degrade the AO7 in water.

Chapter 5: Nitrogen functionalized biochar as PMS activator for AO7 removal

This chapter describes the preparation and characterization of N-doped biochar from saw dust and urea. The performance of the N-doped biochar as PMS activator for AO7 removal was also reported in this chapter. The mechanism of PMS activation and extent of mineralization are also outlined.

Chapter 6: Conclusions and recommendations

This chapter summarizes both of the research results from Chapter 4 and Chapter 5. In addition, some recommendations for future research such as the use of other type of biowaste as precursor for catalyst preparation and heteroatom co-doping are also provided.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced oxidation processes based on catalytic PS activation

AOPs is an advanced treatment method using reactive radicals to degrade recalcitrant organic pollutants [46–48]. Compared to other advanced treatment technologies like membrane separation and carbon adsorption, AOPs generally has more advantages such as (i) no secondary waste in final degradation products, (ii) effective at extreme operating conditions, (iv) ability for selective targeting of desired contaminants, and (v) capable of achieving complete mineralization [47–49]. The application of AOPs technologies such as persulfate-based oxidation, Fenton, electrochemical, ozonation, and photochemical oxidation has been widely used in environmental decontamination. From all mentioned above, persulfate-based oxidation involving PDS and PMS activation AOP-PS for aqueous organic pollutant degradation is gaining a lot of attention due to its versatility and ease of operation [37–39].

Some studies showed that AOP-PS can be employed to effectively degrade different kinds of contaminants such as antibiotics [50], ciprofloxacin [51], acid orange 7 [52], carbamazepine [53], and bisphenol A [54]. Generally, PDS or PMS are used as the oxidant to produce reactive radicals in AOP-PS system. To date, the development of AOP based on PMS activation as applicable technologies for organic contaminant removal has gaining a lot of attention [45-47, 55]. In the oxidizing process of organic pollutant and achieving complete mineralization, generally PMS need to be activated to generate reactive oxygen species (ROS) [56]. There are some methods to activate these oxidants such as using catalyst, heat, chemicals, base, and ultrasound. The catalytic PS activation approach is the most efficient method compared with others because of its low cost and simple preparation during reaction [45]. The use of catalyst to activate persulfate is better to occur in the heterogeneous systems compared to homogenous systems due to the advantages such as ease of catalyst recovery and there is no need for further treatment to remove the dissolved metals after treatment. In addition, this system can be operated under extreme conditions such as high pressure and temperature utmost conditions [57]. Furthermore, the heterogeneous system is working well with wide range of pH while the homogeneous system is only works in specific pH range [58].

Previous studies show the using of heterogeneous cobalt oxide as the effective catalyst in the PMS activation process [41–42]. However, the disadvantage of cobalt catalyst related to the leaching problem which leads to the toxic and carcinogenic agent was discovered [43–44]. This was the main reason for researchers to shift their focus on another metal catalyst such as iron-, manganese-, and copper-based catalyst. Nonetheless, the leaching problem is still an issue for these metal catalysts [45]. Hence, the alternative to resolve this problem is needed. One possible approach is to employ carbon-based catalyst, which completely eliminate the use of transition metal-based catalyst.

2.2 PMS catalytic activation using carbon-based catalyst

The carbon-based catalyst can be an environmentally friendly alternative to replace metal-based catalysts. Various carbon-based catalysts with excellent catalytic efficiency and stability, namely activated carbon [59–62], graphene [63–67], carbon nanotubes [68], ordered mesoporous carbon [69], and nanodiamonds [70] have been reported in the literature. This literature review below summarizes the recent efforts that have been made so far toward the development of carbon-based catalysts in environmental applications.

2.2.1 Activated carbon

Lignocellulosic and coal can be applied as a parent material to prepare activated carbon. The activated carbon can be classified into four classes according to the physical characteristics such as its size and shape, namely activated carbon cloth (a kind of activated carbon fabric) [71], activated carbon fiber, granular activated carbon, and powdered activated carbon [72]. The GAC/PMS system was investigated by Zhang et al. [60] for AO7 removal indicating that the GAC surface can host functional groups to activate PMS (Figure 2.1). The system has effectively degraded the pollutant and its kinetics activity follows pseudo-first order reaction. Saputra et al. [61] investigated the degradation of phenol by using H_2O_2, PDS, and PMS as the oxidant and they reported that thermal treatment was needed to recover the used AC capability as PMS activator. Modified AC using ammonia was successfully synthesized by Yang et al. [62]. The catalytic ability and the function of the surface functional group were investigated. It was believed that the correlation between π-π and the pyrrolic group were responsible for improving the AC. Based on some reviews above, AC is proven applicable as PMS activator for pollutant removal.

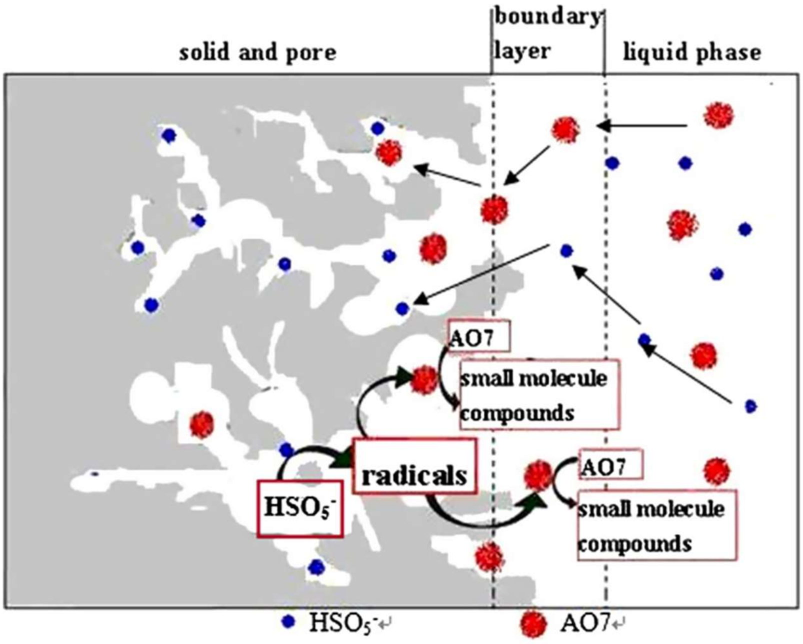

Figure 2.1: Illustration of the simplified reaction pathways for AO7 degradation by GAC/PMS oxidation [60].

2.2.2 Graphene

Graphene is one of the carbon allotrope that has unique electronic clouds consisting of sp^2 and sp^3 hybridized carbon in hexagonal lattice [73]. It has high SSA, mobile electrons, the intrinsic ability to conduct heat, and excellent mechanical force. Various attempts to developed graphene as an efficient PMS activator have been conducted. For instance, Duan et al. [66] successfully synthesized S and N co-doped graphene using one-pot synthesis technique where all the reactants put altogether into one reactor. By applying sulfur as nitrogen co-dopant, positive results in improving activity of PMS activation for catalytic oxidation of pollutant were obtained due to the synergistic interactions between two dopants (Figure 2.2). Several researchers [73, 74] investigated reduced graphene oxide (rGO) activation using CO_2 and it show the great performance as PMS activator for pollutant removal due to its large SSA and oxygen content [76]. The rGO itself is a form of carbon materials which is produced via reduction process of graphene oxide to obtain a graphene pristine's look alike materials [77].

The N-doped rGO was prepared and its performance was studied by Wang et al. [78]. It was found that the N-doped rGO can be used to activate PMS via radical and nonradical pathways, leading to the degradation of pollutants such as phenol, chlorophenols, and dyes. Similarly, a facile approach via annealing method was applied by Duan et al. [65] to get graphene with nitrogen doping. The N-doped amount at 6.54 at. % was obtained. Increasing PMS dosage can enhance degradation reaction by providing more active radicals. Similarly, since higher temperature reactions could give more energy for particles to collide each other on the reaction and speed up the degradation process, increasing temperature could increase phenol removal. However, the stability test shows that after the first time used, the catalyst's performance dropped drastically and effort using heat treatment only restores part of the capability of the catalyst.

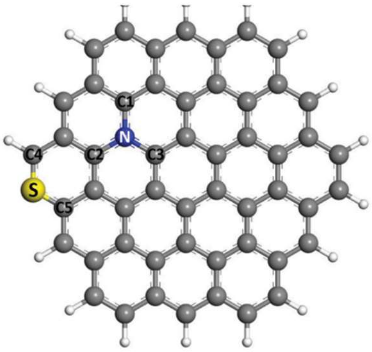

Figure 2.2: Molecular model of S, N-co-doped graphene [66].

2.2.3 Carbon nanotubes

Carbon nanotubes are a type of carbon which consists of cylinder 2-50 graphite sheets. CNTs has a unique properties such as excellent mechanical, structural, and electrical properties that come from carbon bonds, their quasi one-dimensional nature, and their cylindrical symmetry [79]. Previously, Duan et al. [78, 79] successfully applied nitrogen as dopant for single-walled CNT via thermal annealing method and the N-doped single-walled CNT showed affinity to activate PMS, PDS, and H_2O_2 [81]. The N-doped single-walled CNT was proved to act as an electron mediator for PDS to generate ·OH by oxidizing H_2O [81]. Liu et al. [82] Study the effect of incorporating nitrogen and sulfur atoms into the CNTs. It was found that massive improvement can be obtained for benzophenone-4 removal via PMS activation.

2.2.4 Ordered Mesoporous Carbon

Ordered mesoporous carbon which has a unique structure such as single size pore distribution, regular arrangement, adjustable size, hydrothermal stability, and high specific surface area [81, 82] can be produced by several synthesis methods and used as PMS activator. Liu et al. [85] Investigated the use of sulfur to doped OMC. It was proved the doping could increase defect structure, SSA, conductivity and density of ordered pores. The application of this sulfur-doped catalyst to degrade p-nitrophenol by using PDS was greatly successful with degradation rate of p-nitrophenol at 82.02%. Reaction mechanism pathway was found to be both radical and nonradical pathways. However, OMC is relatively expensive and require tedious preparation process to increase its reactivity for PMS activation.

2.2.5 Nanodiamonds

Nanodiamonds with functionalized surface consisting of relatively high sp^3-bonded carbon hybridized nanocrystal (Figure 2.3) have been employed as PMS activator [70, 84]. For example, Yun et al. [87] prepared nanodiamonds at low calcination temperature (500°C) and proved that the nonradical pathway involving

PMS activation via electron transfer from organic molecules to PMS was the main activation mechanism. In another study, Duan et al. [78, 86, 87] synthesized nanodiamonds via thermal annealing method and it was applied to activate PDS for organic pollutants degradation. The uppermost layer on the catalyst surface is the main site to provide the water oxidizing reaction and to form a volatile intermediate. The charge transfer process between water or hydroxide ions and PDS was found to occur in the defect sites of the graphitic structure of the nanodiamonds catalyst. The defective edges of the catalyst play the main role to exhibit radical and nonradical pathways. Even though nanodiamonds can effectively degrade the pollutant via PDS oxidant activation, the expensive preparation method becomes the main concern since a detonation technique and thermal treatment were needed.

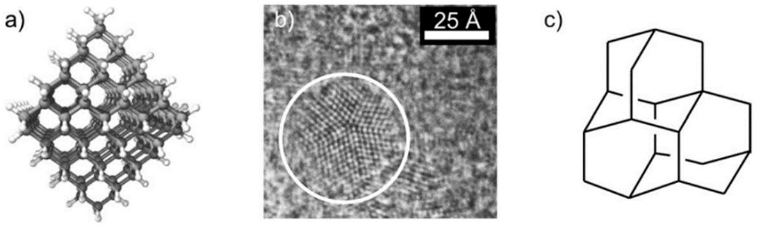

Figure 2.3: (a) Octahedral nano diamond model, (b) meteoritic diamond with multiple twinning, (c) triamantane, a diamondoid molecule [70].

2.2.6 Biochar

Biochar is a solid carbonaceous material obtained as the end product from the process of biomass thermochemical transfiguration [90]. In recent years, biochar has gained extensive attention as a cost-effective precursor for carbon-based catalyst development. Table 2.1 summarizes the preparation method and performance of various biochar-based catalysts as PMS activator for organic pollutant degradation. In general, biochar can be obtained by pyrolysis of biowaste at a various temperatures from 300-700˚C under inert conditions [89–91]. Depending on the precursor used, the biochar obtained through this approach may content high oxygen functional groups. These oxygen functional groups are conducive to PMS/PDS activation. The pyrolysis parameters such as temperature, particle size, heating rate, pressure, and holding time will greatly influence the characteristics of the biochar [94]. Similarly, the type of biowaste precursor used can also affect the physicochemical properties of the biochar [95].

Previously, wood-based biochar was successfully used as PDS and PMS activator to degrade the various pollutants such as AO7 and clofibric acid, with removal efficiency 99.6%, 96%, and 97.8% from studies [89–91], respectively. Other studies reported the use of sludge [96] and corn starch [97] as precursor to produce biochar and the catalysts effectively activated PMS to completely degrade triclosan, trimethoprim and norfloxacin. These studies showed that pristine biochar can be potentially used for pollutant degradation efficiently, resolving the high-cost issue faced by the use of other carbon-based catalysts including graphene, carbon nanotubes and nano diamonds. However, pristine biochar still has disadvantages such as the partial inertness toward for redox catalysis and poorer reusability. Hence improvement of the catalyst performance is still needed. The modification to improve the performance of the pristine biochar can use doping with heteroatom. Doping with heteroatom such as nitrogen, sulfur and boron can enhance the catalytic performance without leading to secondary pollution.

Table 0.1:Pristine and modified Biochar and its applications on pollutant degradation.

Type	**Source**	**Modification**	**Pollutant/ Oxidant**	**Reactive Species**	**Findings**	**References**
Biochar	Mesocarp of tangerine peels Epicarp of tangerine peels	Unmodified	Phenols/ PMS	$^1O_2$	• Pyrolysis temperature = 350˚C - 900˚C; t= 90 min • The C=O group has a key role in $^1O_2$ generation • Both $^1O_2$ and electron transfer are responsible for the mechanism process. • The optimal pyrolysis temperature is at 900˚C • The biochar from mesocarp tangerine peels give better performance than biochar Epicarp tangerine peels • The complete degradation was achieved within 10 min	[98]
Biochar	Sawdust of poplar	Unmodified	AO7/ PDS	$SO_4^{\cdot-}$, $\cdot OH$	• Pyrolysis temperature = 700˚C; t= 120 min • PDS can be activated excellently by wood-based biochar. • The generation of reactive radicals was affected by C-OH and π-electron density. • Removal efficiency = 99.6% in 14 min.	[91]
Biochar	Sawdust	Unmodified	AO7/ PS	$SO_4^{\cdot-}$, $\cdot OH$	• Pyrolysis temperature= 300˚C - 700˚C; t= 120 min; heating rate= 10˚C/ min. • Pseudo –first-order kinetics. • Rate constant = 174.0 x $10^{-4}min^{-1}$. • Removal efficiency = 96%	[93]
Biochar	Sawdust	Unmodified	CA/ PDS	$SO_4^{\cdot-}$, $\cdot OH$	• Pyrolysis temperature = 400˚C - 700˚C • Surface bound reactive radicals play a dominant role. • Removal efficiency = 97.8% in 60 min.	[92]
Porous carbon aerogel	Ammonium persulfate, D-glucose and aniline	Aerogel-modification	Phenol/PS *p*-diphenol/ PS *p*-chloropheno ls/ PS	-	• Calcination temperature = 800˚C; t= 120 min; heating rate= 10˚C/ min. • Removal efficiency = 99.9% in 120 min.	[99]

			p-nitrophenol/ PS Tetracycline / PS Rodhamine B/ PS Safranine T/ PS Malachite green/ PS			
Biochar	Corn stalk	Unmodified	NOR/ PS	$SO_4^{\cdot -}$, $\cdot OH$(minor) $^1O_2$(minor)	• Pyrolysis temperature = 500˚C; t= 90 min; heating rate= 4˚C/ min. • The surface of biochar is the active site for the degradation process of NOR. • Degradation process affected by pH due to the NOR adsorption process on biochar surface. • The mechanism of degradation process via a nonradical pathway. • Removal efficiency = 94.21% in 300 min.	[97]
Graphitic biochar	The wetland plants (Reed)	N- doping	Orange G / PDS phenol / PDS, sulfamethoxazole / PDS BPA / PDS	$^1O_2$(main) $SO_4^{\cdot -}$, $\cdot OH$ (minor)	• Pyrolysis temperature = 400˚C- 1000˚C; t = 90 min; heating rate = 15˚C/min. • The reaction involving the catalyst from moderate temperature (N-BC400) is based on a radical system while the using catalyst from higher temperature (>700˚C) in the reaction shows the nonradical pathway (oxidative system). • First-order kinetics. • Removal efficiency = 100% in 20 min. Phenol; k= 0.206 min^{-1} SMX; k= 0.214 min^{-1} BPA; k= 0.184 min^{-1}	[100]
Porous carbon	Co substituted ZIF-8	Co and N- doping	Phenol/ PMS	$SO_4^{\cdot -}$ (primary radicals), $\cdot OH$	• Pyrolysis temperature = 1000 ˚C; t = 180min; heating rate=5˚C/min. • Co and N doping synchronically increase the surface active sites of the catalyst.	[101]

					• Pseudo-first-order kinetics. • Removal efficiency = 100% in 50 min.	
Hierarchically ordered porous carbon (HOPC)	Polyaniline (PANI) as a precursor SiO_2NPs as a template for mesopores $ZnCl_2$ for *in situ* micropores production.	N-doping	Phenol/ PMS	$SO_4^{\cdot -}$, $\cdot OH$	• Calcination temperature = 800˚C; t= 60 min • The synergistically effect of SiO_2 and $ZnCl_2$ is useful for the synthesis of hierarchically porous carbon with large S_{BET} and rich pore. • First order kinetics. • 99.2% removal efficiency in 5 min. Rate constant= 1.30 min^{-1}.	[102]
Graphitic biochar	Tannin acid (TA) + Urea+$ZnCl_2$	N-doping	BPA/ PMS	$^1O_2$	• Pyrolysis temperature = 700˚C; t= 60 min; heating rate= 5˚C/min. • Singlet oxygen plays a key role during degradation reactions. • Significantly, the study shown the inhibiting effect of anions, which acted as an important step under high salinity conditions for environmental treatment. • Pseudo- second-order kinetics. • Activation energy = 30 KJ/mol. • 98% removal efficiency in 4 min.	[103]
Biochar	Coffee ground, sawdust, banana peel, orange peel, dried leaves.	N- doping	BPA / PMS	$^1O_2$ $SO_4^{\cdot -}$, $\cdot OH$	• Pyrolysis temperature = 1000 ˚C; t= 60 min; heating rate= 10˚C/ min. • N-doped biochar were produced from biowastes. • N-doped biochar shown excellent BPA degradation via PMS activation. • Singlet oxygen was identified as the dominant ROS. • PMS activation is via nonradical pathway. • Pseudo- first order kinetics.	[104]
Biochar	Human hair	Nitrogen and sulfur co-doped carbon (NSC)	BPA/PMS	$^1O_2$(main active species)	• Pyrolysis temperature = 700˚C, 800˚C, 900˚C; t= 60 min; heating rate= 2˚C/ min. • $^1O_2$is a dominant species in the nonradical pathway.	[105]

				$SO_4^{\cdot -}$, $\cdot OH$(very limited)	• Removal efficiency = 98.4% in 60 min.	
Biochar	Rice straw	N- doping, S-doping (modified biochar)	Metholaclor / PMS	$SO_4^{\cdot -}$, $\cdot OH$	• Pyrolysis temperature = 400˚C - 1000˚C; t= 240 min; heating rate= 15˚C/ min. • N-doping gives a good effect while S-doping shows a negative effect on biochar catalytic activity. • Pseudo –first-order kinetics.	[106]
		Unmodified biochar		$^1O_2$		
Porous Carbon	A biomass-derived Schiff-base polymer	N-doping	4-CP/ PMS	$^1O_2$	• Calcination temperature = 700˚C; t= 120 min. • Pseudo- first order kinetic.	[107]
Graphitic biochar	Peanut shell biomass	Iron-doped	Estrogen/ PS	$SO_4^{\cdot -}$, $\cdot OH$	• Pyrolysis temperature = 400˚C & 900˚C; t= 120 min; heating rate= 5˚C/ min. oxidative species was $^1O_2$. • The use of CoO nanodots improves the electron donor to activate PMS. • Fe-doped graphitic biochar was synthesized via one-step method. • Porous graphitic carbon and iron doping give synergistic effects. • The radical pathway was determined as a mechanism of PS activation y the catalyst. • Removal efficiency = 87% in 90 min.	[108]
Porous carbon	EDTA- 2k	N-doping	SMX/ PS	$\cdot OH$, $SO_4^{\cdot -}$, $O_2\cdot{-}/{}^1O_2$	• Pyrolysis temperature = 600˚C - 800˚C; t= 60 min; heating rate= 5˚C/ min • The optimum performance was given by carbon that prepared at temperature 800˚C. • The radical and nonradical pathways play each role for the mechanism to activate the oxidant. • Calcination regeneration was used to revive the catalyst strength. • Removal efficiency = 99.5% in 120 min.	[109]

Mesoporous carbon	Benzyl disulfide and sucrose. SBA-15 as a hard template.	S- Doping	*p*-nitrophenol/ PS TC (tetracycline / PS SMZ (sulfamethazine) /PS	·OH(dominant), $SO_4^{\cdot-}$, $O_2^{\cdot-}$	• Pyrolysis temperature = 900˚C; t= 3 h; heating rate= 3˚C/ min • The optimum performance can be obtained at room temperature and neutral pH. • PS activation via Radical and nonradical pathways. • The catalyst ability was affected by surface functional groups and defect structure. • Removal efficiency = 91.63% • Pseudo- first order kinetic.	[110]
Biochar nanosheets	Candida utilis	N- doping	BPA/ PMS	$SO_4^{\cdot-}$, ·OH $^1O_2$ (dominant ROS)	• Pyrolysis temperature= 700˚C; t= 2 h; heating rate= 5˚C/ min. • The eco-friendly approach was used to synthesize N-doped biochar nanosheets which show great performance to degrade organic pollutants via PMS activation. • Removal efficiency = 100% • Pseudo- first order kinetic. k= 1.36 min^{-1}	[111]
Fe-impregnated biochar	Maize straw Wheat straw Peanut shell	Fe	SMX/ H_2O_2	·OH	• Pyrolysis temperature = 350˚C - 700˚C; t= 2 h; heating rate= 10˚C/ min. • Degradation was measured via the extraction method. • C-OH and other nonradical sites play a key role in the systems. • Removal efficiency = 99% in 120 min • Pseudo- first order kinetic. K = 0.059 min^{-1}	[112]

2.3 Heteroatom doping

Heteroatom doping for various carbon-based catalysts such as biochar, graphene, CNT, OMC, AC, and nanodiamonds has gained a lot of attention as a means to improve the catalytic properties of carbon materials [62, 79, 80, 83, 102, 111]. The heteroatom doping with boron, sulfur and nitrogen can improve the capability of carbon-based catalyst as PMS activator.

2.3.1 Boron doping

Boron is one of the most suitable dopants for carbon heteroatom doping. It is because boron has lower penetration barrier (1.3 eV), make it easier to pass through carbon atom during doping process [114]. Several approaches have been developed to prepare B-doped catalyst. For example, thermal annealing method, chemical vapour deposition [115], and bottom up approach [116]. Liu et al. [117] developed B-doped graphitic porous biochar to activate PDS for sulfamethoxazole degradation. They prepared B-doped biochar catalyst using annealing method. They found out that B-doped graphitic biochar/ PDS systems can degrade 94% of sulfamethoxazole effectively in 120 min.

2.3.2 Sulfur doping

Various approaches have been applied to synthesize S-doped carbon materials such as direct annealing treatment of GO and benzyl disulfide under argon environment [118], chemical vapor deposition [115], thermal treatment, thermal exfoliation, ethanol- thermal reaction, hydrothermal treatment, arc discharge, microwave assisted, solvothermal method, microwave-assisted solvothermal method [119]. In general, sulfur has similar electronegativity ($\chi_S = 2.58$) with carbon ($\chi_c = 2.55$) [120] and can positively influence the carbon matrix for enhanced catalytic activity.

The sulfur species is able to share the conjugated planar system in the carbon structure by created a bonding with benzene rings [121]. The large size of sulfur can also induce more structural defects within carbon crystal lattice, thus provide more edge-active sites [122].

Mohapatra at al. [123] developed S-doped carbon-based catalyst utilizing facile-flame pyrolysis technique. The resultant product has a high specific surface area (950 m^2 g^{-1}), high S-content (~3.6 at. %) and ordered mesoporous structure (~3.9 nm). The product was applied as super capacitor electrode in symmetric device configurations [123]. Petit et al. [124] synthesized two carbons with different sulfur contents and oxidized the materials using chemical treatment or air heating. They applied the product on arsine adsorption. It was found that the adsorption capacities of C-1 and C-2 carbon is 2.7 mmol g^{-1} (211 mg g^{-1}) and 1.0 mmol g^{-1} (78 mg g^{-1}), respectively [124].

2.3.3 Nitrogen doping

Nitrogen doping creates redox active-functional groups to form the electron states and the surface active sites within the carbonaceous matrix [125]. The electronic state of the adjacent carbon atom towards electron acceptor molecules were improved by the formation of pyrrolic N, pyridinic N, and graphitic N from nitrogen doping. This electronic states is important for electron transfer reaction [124–126]. Graphitic N is the main active sites for PMS activation and it is believed to be the active site to generate $^1O_2$ through nucleophilic addition of PMS during nonradical oxidation pathway [129].

Oh et al. [129] employed spent coffee ground as a biowaste precursor to prepare N-doped biochar. The N-doped biochar was used as PMS activator to degrade bisphenol A in aqueous system. The N-doped biochar prepared at 1000 °C possessed the highest catalytic activity due to an excellent degree of graphitization, its relatively high surface area, and optimum N configurations. Various biowastes (sawdust, banana peel, orange peel, dried leaves and spent coffee waste) have been studied as precursor [104] to prepare N-doped biochar for BPA degradation via PMS activation. Sawdust and spent coffee ground were found to have high graphitic N and largest specific surface area at around 44–46 at% and >400 $m^2 g^{-1}$, respectively.

Li et al. [113] developed N-doped porous biochar by using *in situ* pyrolysis technique. They used corn stalk as a parent material and using urea as a nitrogen source. Besides that, they applied $NaHCO_3$ as an activation agent that has synergistic effect with urea in increasing the pore structure in biochar. The results from the phenol removal via adsorption by applying the biochar catalyst that produced at 700°C showed a rapid adsorption occurred at the first 60 min, then slow down until 480 min. moreover, at 720 min, the adsorption equilibrium was achieved [113].

Owing to its effectiveness in modulating graphitic structure and properties while maintaining high electrical conductivity, nitrogen is a preferable dopant compared to boron and sulfur doping. Additional π-electrons in a graphitic plane can be provided by N doping using its excessive valence electrons and together with the electronegativity difference between N and C, a reduced work-function, high surface energy and tunable polarization of graphitic carbons can be obtained. Due to these reason, the modification electrical properties and surface reactivity of N-doped sites can be utilized for many relevant application of graphitic carbons, such as energy storage devices, flexible electronics, and catalysts [130].

2.4 Mechanism

Basically, the PMS activation mechanism by carbon-based catalyst involves radical and nonradical pathways. The radical mechanism in refers to the generation of reactive species such as $SO_4^{\cdot -}$ and $^{\cdot}OH$ from the interaction of PMS and catalyst. Figure 2.4 shows the mechanism of PMS activation on carbon-based catalysts which consists of radical and nonradical pathways. The type of PMS activation mechanism will determine the kind of reactive species generated in the system for pollutant removal. These reactive species are excellent oxidizing agent and can be used to destroy pollutants in water [131]. Meanwhile, the nonradical mechanism includes the formation of activated oxidant-catalyst complex, surface-bound radicals, and singlet oxygen generation. Compared to the radical mechanism, nonradical mechanism is more selective to the electron-rich species and the catalytic activity is dependent on the texture and adsorptive capacity of the organic substrates as well as the properties of the catalysts.

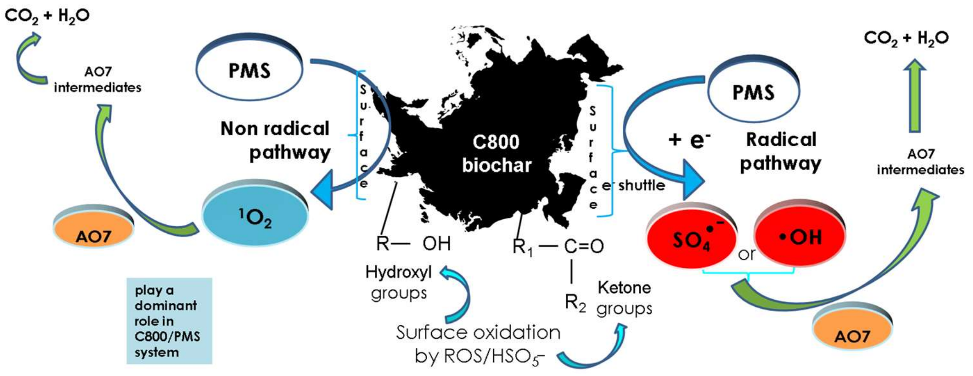

Figure 2.4: Proposed mechanism of PMS activation on carbon-based catalysts.

2.5 Summary of literature review

In summary, this chapter reviews the trend of carbon-based catalyst especially biochar for pollutant degradation via PMS activation. Biochar modification using boron, sulfur and nitrogen have been discussed. The mechanism of PMS activation and pollutant degradation was briefly reviewed in this chapter. While various carbon-based catalysts have been identified as possible PMS activator, several challenges exist, namely the high cost and inertness of the catalyst. Moreover, knowledge on the development of the scalable and efficient method to prepare N-doped biochar is still lacking. The next chapter within this thesis will discuss an investigation of the pristine biochar-based catalyst and N-doped biochar-based catalysts as potential low cost and efficient PMS activator for pollutant removal.