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PAPER

Nickel azamacrocyclic complex activated persulphate based oxidative degradation of methyl orange: Recovery and reuse of complex using adsorbents

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Adsorbents are useful for the removal of metal complex based catalysts from reaction medium. Moreover, effective catalysts may be recycled with the use of adsorbents. These facts inspired us to investigate the use of adsorbents for the recovery and reuse of a metal complex that could activate persulphate to effectively degrade an organic pollutant in water. Here, we report the nickel complex (C1) activated persulphate based degradation of methyl orange (MO) in water and the removal of C1 using activated carbon (AC) and amberlite (Am) as adsorbents. C1 adsorbed onto AC (C1-AC) was reused in solid form to activate persulphate and degrade MO without leaching of C1 into water. Additionally, solid C1-Am recovered from the degraded MO solution was ion exchanged using sodium chloride to obtain C1 that was reused for MO degradation. The study demonstrates the application of adsorbents such as AC and Am for the adsorptive recovery and reuse of a metal complex based persulphate activator.

Introduction

Adsorption of homogeneous catalysts onto solid supports is useful for recovery and reuse of catalysts.[1-4] Remarkably, metal complexes adsorbed onto solid supports via non-covalent bonding such as π- π [5, 6] and ionic interactions,[2, 7] have been shown as solid reusable catalysts for reduction[7] and oxidation of organic compounds[2, 6, 8] in presence or absence of peroxides.

On the other hand, homogeneous metal ions and complexes are excellent for activation of peroxo compounds such as peroxides (hydrogen peroxide and alkyl peroxides),[9, 10] and persulphates (peroxydisulphate and peroxymonsulphate)[11-15] to generate highly reactive radical oxidants that cause rapid, oxidative degradation and mineralization of organic pollutants in wastewater.[12-21] Particularly, persulphate activation by homogeneous transition metal ions and complexes have gained attention as an advanced oxidation process (AOP) for the degradation of organic pollutants such as dyes [13, 14, 16], antibiotics,[17] pesticides,[18] and cyanobacterial toxins[12, 20] in water.[21]

Earlier, we have reported that the complexes such as a redox active nickel(II) azamacrocyclic complex, (C1, Chart 1), (L=1,8-dimethyl-1,3,6,8,10,13 hexaazacyclotetradecane), and a photoredox active [Ru(II)(bpy)₃]²⁺ complex (where bpy= bpyridine), were useful for activation of persulphate (KPS, potassium persulphate, K₂S₂O₈) that effectively degraded persistent, carcinogenic organic dye pollutants in water.[13, 14] Homogeneous redox active nickel complex C1 activated the persulphate anion, via ion pair mechanism with generation of reactive sulphate radical, hydroxyl radical and trivalent nickel 290 nm species that oxidise organic pollutant (reaction 1-7).[13, 22, 23] It should be noted that transition metal ions, and metal complexes are leftover in water after the degradation of organic pollutants by activation of persulphate.

Recovery and reuse of heterogeneous persulphate activators, with minimal release of metal ions during the persulphate activation and degradation of organic pollutants have been studied. Mainly, these heterogeneous activators were prepared by methods involving wet impregnation, doping, co-precipitation, and calcinations and covalent modifications.[16, 24-28]
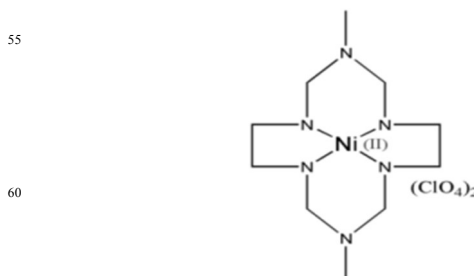
Chart 1. Structure of C1, 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane.

$$[Ni(II)L]^{2+} + S_2O_8^{2-} \leftrightarrow \{Ni(II)L^{2+}+, S_2O_8^{2-}\} \quad (1)$$
$$\text{ion} - \text{pair}$$

$$\{Ni(II)L^{2+} + S_2O_8^{2-}\} \rightarrow [Ni(III)L(SO_4)]^+ + SO_4^{\bullet-} \quad (2)$$

$$[Ni(II)L]^{2+} + SO_4^{\bullet-} \rightarrow [Ni(III)L(SO_4)]^+ \quad (3)$$

$$SO_4^{\bullet-} + \text{Organic Pollutant} \rightarrow \text{Oxidative degradation} \quad (4)$$

$$SO_4^{\bullet-} + H_2O \leftrightarrow OH^{\bullet} + H^+ + SO_4^{2-} \quad (5)$$

$$OH^{\bullet} + \text{Organic Pollutant} \rightarrow \text{Oxidative degradation} \quad (6)$$

$$[Ni(III)L(SO_4)]^+ + \text{Organic Pollutant}$$
$$\rightarrow [Ni(II)L]^{2+} + SO_4^{2-} + \text{Oxidative degradation} \quad (7)$$
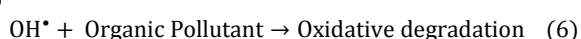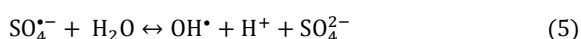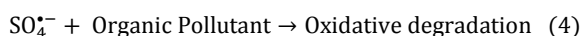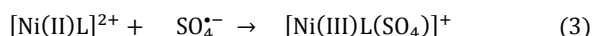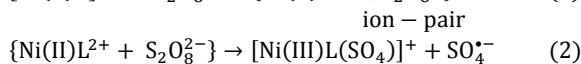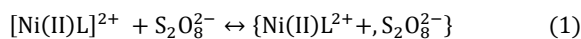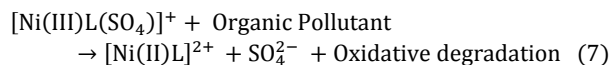
Where,

$[Ni(II)L]^{2+} =$ C1 with nickel in divalent state with absorption maximum at 446 nm;

$[Ni(III)L(SO_4)]^+ =$ C1 in trivalent form with absorption maximum at 290 nm

Notably, adsorbents are useful for the removal of metal ions from wastewater, and for the easy separation of effective metal based catalysts.[29-31] Moreover, adsorbents may be useful to recycle the effective catalysts[32-34], as mentioned above. These facts inspired us to employ adsorbents in a metal complex activated persulpahte based AOP for the recovery and reuse of the complex.

Earlier, it has been reported that nickel azamacrocyclic complexes adsorbed onto solids showed redox reactivity.[35,36] These reports indicated that a nickel azamacrocyclic complex adsorbed onto supports would react with persulphate, and act as reusable solid persulphate activator. Importantly, adsorbents such as Activated carbon (AC)[29-31] and Amberlite (Am) [32-34] have been used to recover metal ions in wastewater, and also to recover and reuse metal complex catalysts. Hence, here we have investigated C1 activated persulphate (KPS) based advanced oxidation process (AOP) to degrade persistent dye pollutant, Methyl Orange (MO), and the adsorptive recovery and reuse of C1 using the adsorbents AC and Am.

Experimental Section

Materials and Reagents. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), Potassium persulphate (KPS, $K_2S_2O_8$), Sulphuric acid (H_2SO_4), Sodium hydroxide (NaOH), Methyl orange, Potassium Iodide (KI), Starch, Sodium Chloride (NaCl), Acetic acid (CH_3COOH), Formic acid (HCOOH), Hydrochloric acid (HCl), Sodium thiosulphate ($Na_2S_2O_3$), Potassium dichromate ($K_2Cr_2O_7$), Ethyl acetate, Tertiary butyl alcohol and Ethanol used were of guaranteed analytical grade, from SD fine chemicals, India. Amberlite[R] IR-120 and Activated Carbon were purchased from SD fine chemicals, India. Nitrogen adsorption–desorption based surface area and pore size values of Activated carbon were found to be 248.8 m²/g and 3.5 nm, respectively, while the surface area and pore size values of Amberlite were 42.1 m²/g and 23.5 nm, respectively. C1 was prepared as reported earlier.[37] Briefly, to a methanolic solution (50 mL) of $NiCl_2.6H_2O$ (1 1.5 g), Ethylenediamine 99% (6.8 mL), Formaldehyde 36% (20 mL), and Methylamine (8.6 mL) were added and stirred at reflux conditions for 24 hour. The resulting orange solution was cooled and filtered. The desired complex was precipitated after adding excess perchloric acid to the filtrate.

For HPLC analysis, acetonitrile (HPLC grade) and Millipore water were used. Stock solutions of MO, complex C1, and KPS were prepared using double distilled water. Simulated ground or natural water was prepared by addition of following components to distilled water as reported earlier: $FeNO_3$ (0.24 µm), $NaHCO_3$ (1.2 mM), Na_2SO_4 (0.34 mM), Na_2HPO_4 (0.28 mM), NaCl (0.86 mM) and resorcinol (1 ppm).[14] Freshly prepared KPS solution was used for all experiments.

Degradation of MO by KPS using C1. For degradation of Methyl Orange (MO), appropriate amount of aqueous MO (20-30 mg/L) solution was taken with and without C1(C1 in the range 12-49 mg/L), and the reaction was initiated by addition of required amount of KPS (5g/L -0.5g/L). Reaction volume was maintained at 5 ml, unless otherwise mentioned. The reaction was carried out at room temperature. Initial pH of the solution was ~7. Degradation of MO was studied by following the decrease in absorption maximum at 464 nm of MO, with respect to time, using JASCO V-570 UV/VIS/NIR spectrophotometer. Degradation of MO by (i) KPS alone (ii) KPS and $Ni(II)Cl_2.6H_2O$ were performed as control experiments. Pseudo-first order rate constant (k) for the degradation of MO was determined from the C/C_0 vs. time plot. Initial concentrations of C1, KPS and MO were varied and (k) values for the degradation of MO were determined. The optimised condition for MO degradation was determined to be MO (20 mg/L), C1 (48.3 mg/L), KPS (1g/L), based on rate constant (k) analysis.

Shimadzu UFLC prominence system with SPDM 20A Prominence diode array detector, equipped with phenomenex C18 HPLC column (250 mm × 4.5 mm, 5 µm) was used for high pressure liquid chromatography (HPLC) analysis. A 70:30 (v/v) mixture of ammonium acetate buffer (pH 4.5)/acetonitrile was used as the mobile phase, in isocratic mode with flow rate of 1 mL/min. For each analysis, 100 µL of sample taken from appropriate reaction mixture was injected and degradation of MO was monitored at 464 nm.

Shimadzu IR-Affinity-1 FT-IR spectrophotometer was used for Fourier transform infrared (FT-IR) analysis of MO degradation. After treatment of MO with KPS and C1, the reaction mixture was completely evaporated using a rotary evaporator. Degraded intermediates present in this dry residue was extracted with ethanol and ethyl acetate and then evaporated to solid residues for FTIR analysis. In the liquid chromatography mass spectrometry (LCMS) analysis, Vantage TSQ triple stage quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with heated electro spray ionization (HESI) was used. The mass spectrometer is coupled with an Agilent 1290 infinity UHPLC system (Agilent Technologies India Pvt. Ltd., India). The UHPLC was provided with column oven (set at 40º C), auto-sampler and a thermo-controller (set at 4°C). A flow through injection mode equipped with a needle wash system was used (with acetonitrile, 0.1% formic acid) before injection to ensure zero percent carry over problems. UHPLC system was equipped with Luna C-18(2) column (4.6 × 150 mm, 5 µm, Phenomenex, Inc). Mobile phase: Solvent A was 10 mM ammonium acetate containing 0.1% formic acid; and Solvent B was acetonitrile containing 0.1% formic acid. Binary gradient was optimized to get maximum separation (Gradient: 5% B at 0 min, 5% B at 3 min, 90% B at 15 min, 0% B at 15-17 min) at flow rate of 300 µL/min. Operating conditions were as follows: spray voltage -4000V; ion transfer capillary temperature-270°C; source temperature- 300 °C; sheath gas-20, auxiliary gas-10 (arbitrary units) and ion polarity negative, full scan analysis- 50 to 400 m/z with the scan time of 500 millisecond. 10µL of sample from appropriate reaction mixture of MO, KPS and C1 was injected after specific time interval.

Sievers 900 TOC analyser was used for Total Organic Carbon

(TOC) analysis during degradation. An aliquot of 20 mL reaction solution was taken at specific time intervals from reaction mixture (100 mL) containing MO (20 mg/L), KPS (1 g/L) and C1 (48.3 mg/L) and injected into TOC analyser.

5 Redox reaction between C1 (48.3 mg/L) and KPS (1 g/L) leading to formation of trivalent nickel 290 nm species was monitored at its absorption maximum at 290 nm, similar to the reaction of tetraazamacrocyclic nickel complex with ammonium persulphate as reported by Haines *et al*., (Figure S 1).[22, 23] C1

10 existing predominantly as trivalent nickel 290 nm species was prepared by incubating the reaction mixture containing KPS and C1 (Figure S 1).[22, 23] Reactivity of trivalent nickel 290 nm species with MO was monitored by following the absorption spectral changes of MO. Concentration of KPS during MO degradation in

15 presence and absence of C1 was determined by iodometric titration as reported earlier.[38,39] Tertiary butyl alcohol and Ethanol were used as scavengers for sulphate and hydroxyl radicals as reported earlier.[11, 40]

Adsorption of C1 onto Activated carbon (AC) and Amberlite
20 **(Am).** Langmuir and Freundlich adsorption equations were used to determine the adsorptivity (K_F and q_m values) of C1 onto AC and Am.[41,42]

$$\text{Langmuir isotherm: } q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

$$\text{Freundlich Isotherm: } q_e = K_F C_e^{1/n}$$

25 q_e = amount of adsorbate adsorbed on to adsorbent (mg/g) at equilibrium; C_e = equilibrium concentration of adsorbate in the solution (mg/L); $q_{m(L)}$ = Langmuir maximum adsorption capacity (mg/g); K_a = Langmuir constant (L/mg); K_F = Freundlich constant indicative of relative adsorption capacity of the adsorbent

30 ($[\text{mg}^{1-(1/n)}.\text{L}^{1/n}]$/g); 1/n = Freundlich constant indicative of intensity of adsorption. Freundlich maximum adsorption capacity was determined from the equation $K_F = q_m / C_0^{1/n}$ where, q_m is Freundlich maximum adsorption capacity (mg/g), K_F is Freundlich constant indicative of relative adsorption capacity of

35 the adsorbent ($[\text{mg}^{1-(1/n)}.\text{L}^{1/n}]$/g), and C_0 is the initial concentration of adsorbate in the bulk solution (mg/L).[41,42]

The equilibrium concentration of the C1 during adsorption was determined by following the absorption of C1. In the absence of

40 KPS, the concentration of the C1 in the divalent state was followed by monitoring the d-d absorption maximum at 446 nm. In the presence of KPS, the concentration of C1 in the trivalent state was followed by monitoring the absorption band maximum around 290 nm.[22, 23]

45 C1-AC was prepared by adding AC (1g) to 100 ml of C1 (4.25 mM). This suspension was stirred overnight. Supernatant obtained after removing AC was filtered using 0.45 μM Polytetrafluoroethylene (PFTE) membrane filter and the absorption spectrum of the filtrate was recorded to determine the

50 adsorption. Then the C1 immobilized onto AC (C1-AC) was removed by filtration and washed thrice with distilled water, and finally dried in a desiccator. The loading of C1 in C1-AC was determined to be 160.6 mg of C1 per gram of AC (16.0 %). Similarly for preparation of C1-Am, Am (1g) was added to 50ml

55 of C1 (4.25 mM). The loading of C1 in C1-Am was determined to be 96.4 mg of C1 per gram of Am (9.64 %). X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific (East Grinstead, UK) θ probe spectrometer and monochromatic Al-Kα radiation (photon energy

60 1486.6 eV). The adsorption of MO onto AC was studied by following the absorbance of MO at 464 nm.

Degradation of MO by KPS using C1 adsorbed onto AC (C1-AC) and Am (C1-Am). Degradation of MO (30 mg/L) by KPS

65 (1 g/L) using C1-AC (0.3 g/L, 16.0 % C1 loading)/C1-Am (0.5 g/L, 9.64 % C1 loading) was studied spectrophotometrically, as mentioned above for homogeneous degradation of MO. Suspension of 0.3 g/L of C1-AC with 16.0 % C1 loading, or 0.5 g/L of C1-Am with 9.64 % C1 loading in reaction mixture (5 ml)

70 corresponds to an effective concentration of 48.3 mg/L of C1, similar to the amount of C1 used in homogeneous condition. Control experiments (i) bare AC/Am (without C1) and MO in presence of KPS (ii) C1-AC/C1-Am and MO in absence of KPS were performed. Reuse of C1-AC for MO degradation was

75 studied by performing cyclic degradation experiment in presence and absence of KPS. After each cycle, C1-AC was removed by centrifugation and reused for the subsequent cycle. Degraded MO solution obtained from each cycle was analysed for the presence of C1 (as nickel) by AAS. Similarly, the reuse of C1-AC for MO

80 degradation in simulated natural water was also performed. The concentration of C1 in the MO degraded solution was monitored by determination of the nickel content using atomic absorption spectrometer (AAS) (Perkin Elmer, AAS 400), as well as by following the change in the absorption of C1. Ion exchange

85 (extraction) of C1 that was adsorbed onto Am was performed by eluting with 0.17 M NaCl solution. Degradation of MO by using the C1 that was extracted from C1-Am was performed similar to the protocol mentioned above.

Results and Discussion

90 **Homogeneous C1 activated persulphate and degradation of MO**. Absorption spectral results revealed that the degradation of MO (20 mg/L) by KPS (1g/L to 5g/L) was slow and incomplete after 60 min of reaction (Figure 1A & B). On the other hand, MO (20 mg/L) was rapidly degraded by KPS (1g/L) in presence of

95 persulphate activator C1 (48.3 mg/L) within 10 min, with a pseudo-first order rate constant value (k) of 3.9 ± 0.07 s^{-1} (Figure 2A & 1B). The effects of initial concentrations of MO, KPS and C1 on k value for the degradation of MO were determined (Table 1). k value increased with increase in the initial concentration of

100 C1, and KPS, however k value decreased with increase in the initial concentration of MO. It was observed that NiCl$_2$.6H$_2$O (without azamacrocyclic ligand) had no effect on the degradation of MO by KPS, unlike redox active C1 (Figure 1B). Thus, these results revealed that the persulphate activator C1 is required for

105 rapid and complete degradation of MO by KPS (1g/L) (Fig. 1B & Table 1).

Further, the MO peak at retention time 11 min observed in HPLC chromatogram, rapidly disappeared in presence of KPS and C1(Figure 2B). However, a prominent MO peak was

110 observed in the presence of KPS alone (Figure 2B). Thus, HPLC results also revealed that the degradation of MO by KPS in

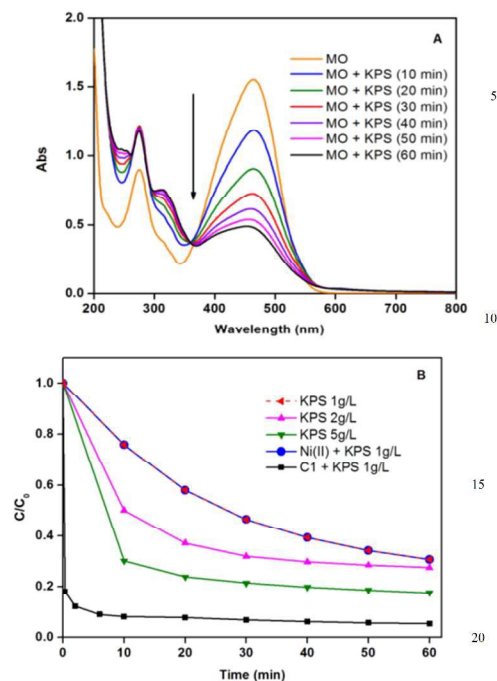presence of C1 was rapid and complete, whereas degradation of MO was slow and incomplete by KPS alone.

Figure 1. (A) Absorption spectra showing the degradation of MO by KPS. (B) C/C0 plot showing degradation of MO in presence of KPS, KPS + C1, and NiCl$_2$.6H$_2$O + KPS. [MO] = 20 mg/L; [C1] = 48.3 mg/L. [NiCl$_2$.6H$_2$O] = 23.7mg/L.
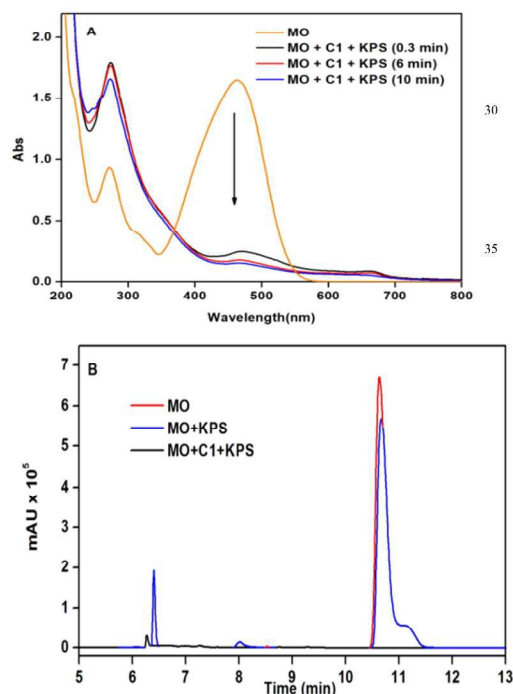

Figure 2. (A) Absorption spectra showing the degradation of MO by KPS in presence of C1 (B) HPLC chromatogram of MO (red), MO degraded by KPS (blue) and, MO degraded by KPS in presence of C1 (black). [MO] = 20 mg/L; [KPS] = 1g/L; [C1] = 48.3 mg/L. Treatment time = 10 min

The N=N- stretching peak at 1608 cm^{-1} of azo group was absent in FT-IR spectra of ethanol and ethyl acetate extract residues of MO degraded by KPS in presence of C1(Figure S 2). Moreover, IR spectra of degraded MO showed peaks at 3000 cm^{-1} and 2785 cm^{-1} due to –C-H stretching; 1223 cm^{-1} because of C-N-stretching; 858 cm^{-1} and 1051 cm^{-1} corresponding to aromatic ring vibrations, and 587 cm^{-1} and 692 cm^{-1} due to –C-S- and S=O stretching, respectively (Figure S 2).[43-45] These IR results indicated the loss of characteristic azo group of MO, and transformation to aromatic amine and sulphonated intermediates during degradation.

Table. 1 Pseudo-first order rate constants determined for degradation of MO by KPS under different concentrations of MO, C1 and KPS.

C1 ppm (mg/L)	KPS (g/L)	MO (mg/L)	Rate constant k (s^{-1})
12.07	1	20	0.55 ± 0.01
24.15	1	20	1.16 ± 0.03
48.3	1	20	3.90 ± 0.07
48.3	0.5	20	1.06 ± 0.03
48.3	2	20	3.82 ± 0.11
48.3	1	50	1.96 ± 0.07
48.3	1	100	0.66 ± 0.02

Room temperature; Initial pH ~7

Total ion chromatogram (TIC) of MO showed a single peak at RT 14.4 min (Figure S 3A) corresponding to 304 m/z of MO (Figure S 4). This MO peak was completely absent in TIC of MO degraded by KPS in presence of C1 (Figure S 3D), whereas a prominent MO peak was observed in TIC of MO degraded by KPS alone (Figure S 3B). Some of the degradation intermediates (Figure S 3 B-D, S 4, Table 2) of MO observed during the reaction are similar to those reported earlier.[46-48] Degradation intermediates 200 m/z (RT 12.5 min) and 290 m/Z (RT 13.7 min) disappeared in TIC of MO degraded by KPS in presence of C1, within 30 min (Figure S 3 C-D), whereas these peaks were clearly observed in TIC of MO degraded by KPS alone even after 60 min (Figure S 3B).

Table. 2. Proposed Degradation Intermediates of MO

min (RT)	Mol. Wt	Proposed Structures
11.6	157	
12.5	200	
13.66	240	
13.7	290	

The loss of MO and significant reduction in the degraded intermediates by KPS in presence of C1 indicated that the combination of KPS and C1 could lead to mineralization of MO. One hour of treatment of MO (20 mg/L) with KPS (1 g/L) in presence of C1 (48.3 mg/L) caused about 75 % reduction of TOC, whereas only 10% TOC reduction was observed after one hour of treatment of MO by KPS alone (1g/L). Thus, the significant reduction in the TOC, revealed the ability of KPS and C1 to effectively degrade and mineralize MO.

Earlier, Haines *et al.,* have reported that the reaction between nickel(II) azamacrocyclic complex and ammonium persulphate rapidly generated sulphate radical, and trivalent nickel 290 nm species, via an ion-pair mechanism (reaction 1-3).[22, 23]Sulphate radical is non-selective and a highly reactive oxidant. It has been shown that sulphate radical can oxidise a wide variety of organic pollutants (reaction 4) such as dyes [13, 14, 16], antibiotics,[17] pesticides,[18] cyanobacterial toxins,[19, 20, 49] as well as microbial pollutants [14, 15] and toxic metal ions.[50] Additionally, sulphate radical also react with water in acidic and neutral conditions to produce hydroxyl radical, which has the potential to oxidise the organic substrates (reaction 5).[11, 13, 21]Rate of degradation of MO by KPS and C1 was retarded in presence of radical scavengers such as tertiary butyl alcohol and ethanol (Figure 3, Table 3), indicating that both sulphate and hydroxyl radicals are involved in the degradation of MO. Similar results were reported for activation of persulphate using metal ions (Fe^{2+},Fe^{3+}, Ag^+) for degradation of halocarbon.[11]

Degradation of MO was also observed for the solution that has C1 predominantly as trivalent nickel 290 nm species in presence of KPS (Figure S 5). Moreover, it was determined by iodometric titration that about 21 % (0.21g/L) of KPS was consumed for degradation of MO (20 mg/L) by KPS (1g/L) in presence of C1 (48.3 mg/L) (with in 10 min), whereas only 4% (0.04g/L) of KPS was consumed for the reaction between MO (20 mg/L) and KPS (1g/L) without C1 (after 60 min of reaction). These results indicate that the trivalent nickel 290 nm species oxidise MO (reaction 7) and reduce to the divalent state. The resulting divalent C1 could be oxidised by KPS (reaction 1-3), leading to higher consumption of KPS (more than the stoichiometric amount of C1), as revealed by titration experiments.
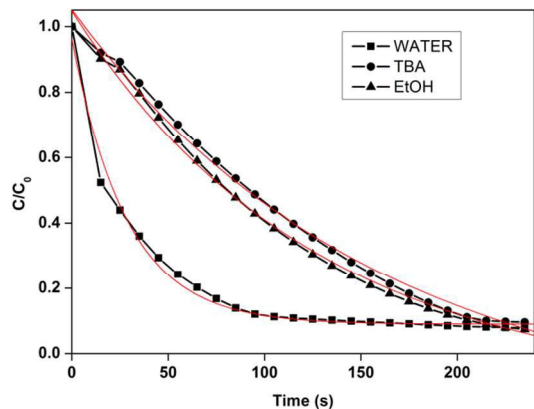

Figure 3. Effect of radical scavengers on the rate of degradation of MO by KPS and C1. [C1] =100μM; [KPS] = 1g/L; [MO] = 50 mg/L; [TBA] = 0.5 M; [Ethanol] = 0.5 M.

Earlier it has been shown that trivalent nickel complexes could oxidise organic substrates (reaction 7).[13, 51, 52] All the above results highlight that C1 has the ability to activate persulphate and cause degradation of MO, as proposed in the reactions 1-7.

Table 3. Degradation of MO by C1 activated KPS in presence of radical scavengers

Scavenger	Pseudo-first order rate constant k (s^{-1})
TBA (0.5 M)	0.38 ± 0.02
Ethanol (0.5M)	0.47 ± 0.01
None	1.96 ± 0.07

[C1] = 100 (mg/L); [KPS] = 1g/L; [MO]= 50 (mg/L).

Although homogeneous C1 activated KPS and degraded MO, it is important to recover the C1 from the solution and reuse. The results on the adsorptive recovery and reuse of C1 using adsorbents for water remediation[29-34] such as AC and Am are presented below.

Recovery and reuse of C1 using adsorbents. Adsorption of C1 onto AC and Am adsorbents were determined to follow Freundlich adsorption isotherm model (Figure 4 & S 6), and their adsorptivity parameters are tabulated (Table 4 & S1). AAS results revealed the absence of C1 in water (not detectable, and less than 1 mg/L) after the recovery of C1 using adsorbents. Thus, AC and Am are useful for adsorptive recovery of C1 in presence of persulphate, where C1 existed as trivalent nickel 290 nm species (Figure 2A & S 5), as well as for the recovery of C1 with nickel in divalent state in the absence of persulphate.

Table 4. Freundlich adsorption isotherm parameters for adsorption of C1 onto Amberlite and Activated carbon in presence and absence of KPS.

Freundlich Adsorption Isotherm

Adsorbent	Adsorbate	K_F	1/n	q_m	R^2
Am	C1[a]	2.27	0.20	6.1	0.989
AC	C1[a]	30.37	0.20	75.8	0.981
Am	C1[b]	8.61	0.33	106.9	0.979
AC	C1[b]	24.06	0.36	375.6	0.964

a= C1 in presence of KPS, b= C1, in absence of KPS; $[C1]_0$ = 2.06 g/L for Am and AC. K_F = Freundlich constant indicative of equilibrium adsorption capacity of the adsorbent ($[mg^{1-(1/n)}.L^{1/n}]/g$); 1/n = Freundlich constant indicative of intensity of adsorption; q_m = Freundlich maximum adsorption capacity (mg/g). R^2 = Correlation coefficient.

X-ray photoelectron spectrum of C1 adsorbed onto AC (C1-AC) showed peaks at 400.3 eV and 855.9 eV that correspond to binding energy of nitrogen, (N1s), and divalent nickel of C1 ($Ni2p_{3/2}$), respectively (Figure 5).[53-59] C1 adsorbed onto Am (C1-Am) also showed similar peaks (Figure S7). The ability of solid C1-AC and C1-Am to activate persulphate and degrade MO was investigated, and the results are presented below.

MO (30 mg/L) was rapidly degraded by KPS (1g/L) in

presence of C1-AC (0.3g/L, 16 % loaded C1) within 10 min,(Figure 6 A) . On the other hand, degradation of MO (30 mg/L) by KPS (1g/L) in presence of AC(0.3g/L of bare AC without C1) was incomplete even after 60 min of treatment, 5 (Figure 6 A).
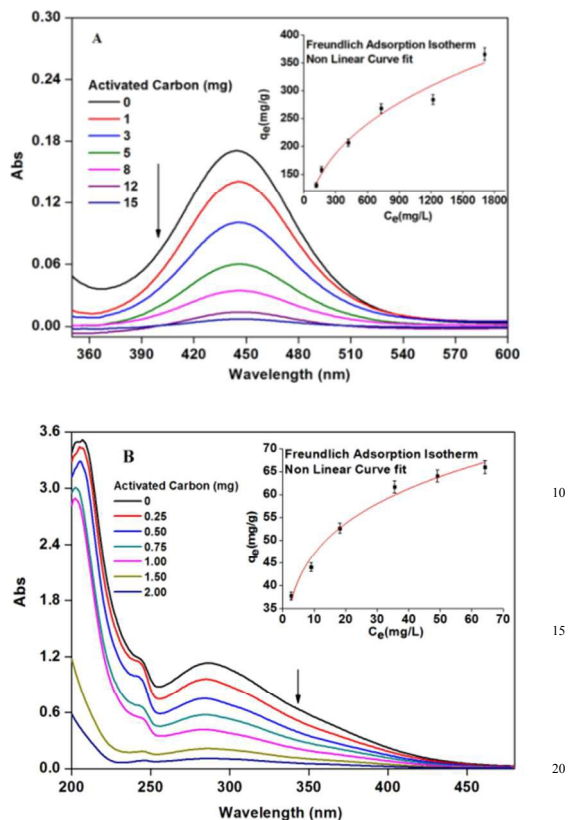

Figure 4. Adsorption of C1 onto activated carbon without KPS **(A)** and with KPS **(B)**. Inset shows the non-linear fitting for Freundlich adsorption 25 isotherm.
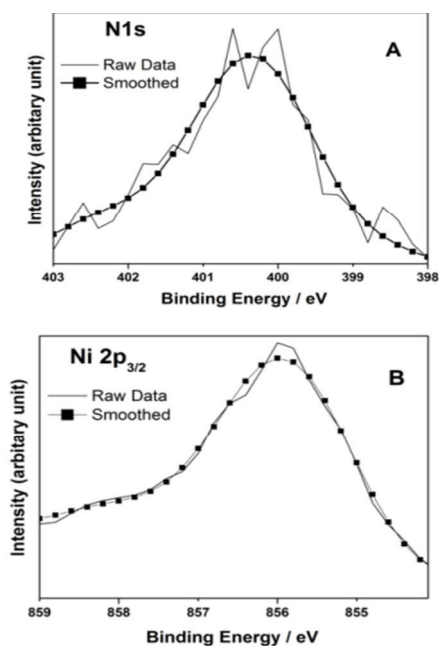

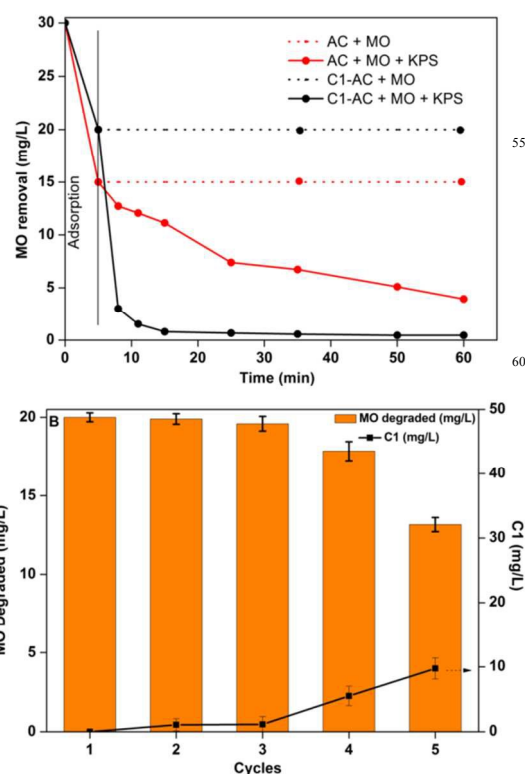**Figure 5.** XPS of C1-AC showing (A) N1s and (B) Ni2p$_{3/2}$ peaks.

Figure 6. (A) Plot showing MO degradation by KPS in the presence of AC and C1-AC. [AC] = 0.3 g/L; [C1-AC] = 0.3 g/L (16% loading; 65 effective concentration of C1 is 48.3 mg/L) ; [KPS] = 1g/L. The dotted lines represent the adsorptive removal of MO by AC and C1-AC in absence of KPS. (B) Reuse of C1-AC. Reuse runs (cycles) for degradation of MO by C1-AC in the presence of KPS, and the corresponding concentration of C1 (in mg/L) at the end of each cycle in 70 the treated solution. Initial concentration of MO at each cycle is 20 mg/L

Further, the adsorption of MO (30 mg/L) onto C1-AC, and AC were determined to be ~ 9 mg/L and 12 mg/L, respectively (Figure 6 A , Table S 2), revealing that the adsorptive removal of MO by C1-AC and AC was incomplete.

75 It was observed that XPS of C1-AC treated with persulphate showed additional peaks at 401.6 eV and 854.8 eV that correspond to nitrogen (N1s), and trivalent nickel of C1 (Ni2p$_{3/2}$) (Figure S 8), respectively.[53-59]Moreover, the iodometric titration results, as discussed earlier, also revealed higher consumption of 80 persulphate (than the stochiometric amount of C1) during the degradation of MO. All the above results i.e both the XPS and iodometric titration results reveal the redox reaction between C1 in solid form and KPS. C1-AC was reused for five times to activate persulphate and degrade MO, in which almost complete 85 degradation of MO was observed for the first three reuse runs without significant loss of C1 from C1-AC (less than ~1 mg/L in each reuse run)(Figure 6B). At fourth and fifth reuse runs, MO degradation was determined to be ~80% and 60%, respectively. Moreover, AAS analysis revealed that there was about 10% (5.52 90 mg/L), and 20% (9.7 mg/L) of leaching of nickel from C1-AC into water at the fourth and fifth reuse runs, respectively(Figure 6B, S9). The reusability of C1-AC was also observed for the degradation of MO carried in simulated natural water (Figure S 10). All the above results reveal that AC is useful to recover C1 95 and reuse C1 as solid C1-AC.
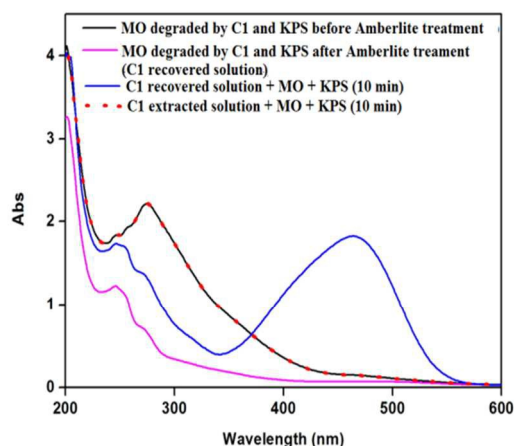
Figure 7. Reusability of C1 using amberlite. [MO] = 20 mg/L; [KPS] = 1g/L; [C1] = 48.3 mg/L; [Am] = 15mg/L

Although, C1 was effectively adsorbed onto Am, the solid C1-Am was not effective to activate persulphate and degrade MO, unlike the solid C1-AC discussed above. It is proposed that the electrostatic repulsion between the negatively charged Am and persulphate anion is not favourable for their interaction to activate the persulphate anion by the C1 adsorbed onto Am. However, the adsorption of C1 onto Am was useful to completely recover the homogeneous C1 from the degraded MO solution, as revealed by absorption and AAS results (Figure 7, Black and Magenta). Further, the recovered C1-Am was ion exchanged using sodium chloride to obtain C1 (> 85% (extracted) as determined from AAS) that was reused for MO degradation. (Figure 7, Red dotted line).

Almost similar results were also observed for the degradation of MO carried in simulated natural water (Figure S 11). Thus, Am was useful in a metal complex activated persulphate based AOP for adsorptive recovery of the complex, and for the reuse of complex in homogeneous form after ion exchange process.

Conclusions

In summary, homogeneous metal complex based persulphate activator, C1, was recovered by adsorption onto AC and Am. C1 adsorbed onto AC (C1-AC) showed the ability to activate persulphate and degrade MO. Moreover, solid C1-AC was reused to activate persulphate and degrade MO without significant leaching of nickel into solution. Additionally, the recovered C1-Am was ion exchanged to obtain C1 that was reused for MO degradation. These results demonstrate the application of adsorbents to recover and reuse a metal complex based persulphate activator.

Recovery and reuse of a metal complex based persulphate activator is advantageous in persulphate based AOP for the treatment of natural or ground water contaminated with recalcitrant pollutants from industries and other sources. The study draws attention to the application of adsorbents in metal complexes activated persulphate based AOP for the removal of metal based persulphate activators from water after the treatment that would prevent the entry of metal ions into water bodies. Moreover, the study highlights the recyclability of an effective metal complex based persulphate activator using versatile adsorbents.

Notes and references

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