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Solid manganese dioxide as heterogeneous oxidant of aniline in the preparation of conducting polyaniline or polyaniline/manganese dioxide composites

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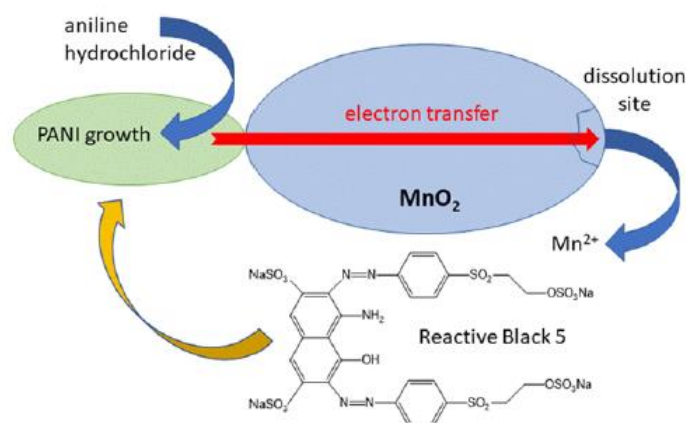
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HIGHLIGHTS

- Aniline was oxidized with solid sacrificial oxidant, manganese dioxide.
- Polyaniline is obtained at $[\text{MnO}_2]/[\text{ani-line}] \leq 1.25$.
- At $[\text{MnO}_2]/[\text{aniline}] > 1.25$, polyaniline/manganese dioxide composites are produced.
- The adsorption of organic dyes on polyaniline and its composites was compared.

GRAPHICAL ABSTRACT



ABSTRACT

Various oxidants used in the preparation of polyaniline are reviewed. Insoluble solid oxidant, manganese dioxide, has been investigated in the heterogeneous synthesis of polyaniline in detail. Aniline was oxidized in acidic aqueous medium at various oxidant-to-monomer mole ratios $[\text{MnO}_2]/[\text{aniline}]$. At $[\text{MnO}_2]/[\text{aniline}] \leq 1.25$, i.e. at and below the stoichiometric composition, only polyaniline was produced, and the solid oxidant was absent in the product due to its reductive dissolution which took place during the reaction. Polyaniline prepared under such conditions did not differ with respect to conductivity from the standard polyaniline obtained with peroxydisulfate oxidant but fused polyaniline nanofibers have been produced instead of a common globular morphology. The composites of polyaniline/manganese dioxide resulted only at $[\text{MnO}_2]/[\text{aniline}] > 1.25$. Spectroscopic methods suggest that the oxidation with excess of manganese dioxide produced polyaniline at higher oxidation state. The presence of manganese dioxide in the products was confirmed by X-ray diffraction and EDAX. The results are important for the understanding of the preparation and properties of polyaniline/

Keywords: Conducting polymer, dye adsorption, polyaniline, manganese dioxide, solid oxidant reductive dissolution

1. Introduction

Polyaniline [1,2] is one of the most famous and widely used conducting polymers with a conjugated chain structure. Polymer combines an organic structure with some properties of semiconductors and displays original features, such as electronic and ionic conductivity, oxidation-reduction ability, and absorption of electromagnetic radiation. Polyaniline responds to external stimuli and its properties change reversibly when an electric potential is applied, in contact with reducing agents, reactive gases or vapours, acid/base media, etc. The polymer has already been used in electronics, energy storage and conversion, and applied for creation of corrosion-protective and conducting coatings [3-8]. Applications extend beyond the field of electrical properties [2] to water-pollution treatment [9] and biomedicine [5,10].

Polyaniline is synthesized by the oxidative polymerization of aniline [1,11]. This is a simple process, but the properties of the resulting products critically depend on the synthesis conditions, such as temperature, reactant concentrations and acidity of the medium [12]. By far the most important reagent for the synthesis of polyaniline is an oxidant [13, 14]. The present study critically assesses various oxidants and concentrates on new type that is insoluble in the reaction medium.

Electrochemical studies demonstrate that aniline oligomers with a heterogeneous structure of constitutional units and low conductivity are formed at oxidation potentials from + 0.3 V to + 0.5 V vs the normal hydrogen electrode (NHE) [15]. The growth of polymer chains with a regular conjugated structure having an electrical conductivity above $10^{-2} \text{ S cm}^{-1}$, however, requires an increase in the oxidation potential to +1.0 V vs NHE. A certain acidity of the reaction medium is also crucial for successful synthesis [12,16,17]. The optimum conditions are at $\text{pH} < 2.5$ when aniline is present as an anilinium cation. At higher pH non-conducting aniline oligomers are dominating products [18]. The use of concentrated strong acids ($> 5 \text{ M}$) also inhibits the polyaniline synthesis.

Ammonium peroxydisulfate is the most often used for the oxidation of aniline. It is a strong oxidant with a standard oxidation potential +2.01 V vs NHE. It is highly soluble in aqueous media and, for that reason, it is preferred to potassium salt. The synthesis using perox-ydisulfate under typical conditions

proceeds quickly within minutes, with high yield and, in the case of acidic aqueous media, with a very low content of the oligomeric fraction. The conductivity of products obtained in acidic media is of the units S cm^{-1} [11]. Nevertheless, the use of peroxydisulfate can lead to polyaniline overoxidation when used in excess, which reduces its conductivity and stability. Another feature of the use of peroxydisulfate is the production of sulfuric acid as a by-product of the reaction [12], which is associated with the mandatory protonation of polyaniline with sulfate counter-ions, albeit incomplete in the presence of other acids. This is not always desirable, for example, when preparing anticorrosive coatings, since the sulfate anion is corrosive.

Other less commonly used oxidants are hexavalent chromium compounds, dichromate and chromate. They are readily soluble in water, the oxidation potential of these agents depends on acidity. At pH 0-1 it is + 1.33 V but it rapidly decreases with increasing pH. When using chromates, the products of aniline oxidation have spectral characteristics of polyaniline [14,19] and conductivity of $0.1\text{-}10 \text{ S cm}^{-1}$. They are formed only under conditions of increased acidity [20,21]. At a lower acidity, oligomers with low conductivity are obtained [22]. Aniline oxidation with hexavalent chromium leads to products that contain trivalent chromium compounds [23] and could be useful as corrosion inhibitors, catalysts and redox-active materials [23,24]. Nevertheless, the use of hexavalent chromium compounds as an oxidant is problematic due to its high environmental toxicity, especially in a water-soluble form. Trivalent chromium compounds incorporated in polyaniline are potentially toxic, although less dangerous than hexavalent chromium.

Cerium(IV) salts have a fairly high oxidation potential (+1.61 V). The oxidation with cerium sulfate leads to the production of poly-conjugated products of polyaniline-like structure, which is confirmed by the spectral characteristics obtained on both doped and dedoped products. However, the yield of polyaniline is only $\approx 50\%$, and the conductivity of the doped form is in the range of $10^{-1}\text{-}10^{-4} \text{ S cm}^{-1}$, which is lower than in the case of peroxydisulfate [14,25,26].

The polymerization of aniline with potassium periodate (+1.20 V) at optimum acidity conditions leads to the production of a polymer with conductivity up to units of S cm^{-1} . Moreover, polyaniline contains high concentrations of iodine [27,28]. Iodine can be included in the polyaniline structure not only as a counter-ion I^- or I_3^- , but also as a substituent of the benzene ring [29]. The incorporation of iodine anion I_3^- into polyaniline synthesis process can be useful, for example, for sensors or dye-sensitized solar cells.

Unlike the oxidizing agents listed above, vanadium pentoxide (V_2O_5) is insoluble in aqueous media. Having the standard oxidation potential + 1.0 V, it is capable of aniline oxidation, thus forming products with conductivity of $10^{-4}\text{-}10^{-1} \text{ S cm}^{-1}$, which is several orders of magnitude higher than the conductivity of V_2O_5 itself [30,31]. The synthesis proceeds under heterogeneous conditions on the surface and in the V_2O_5 channels of the hydrogel host. Evidence for the formation of polyaniline inside V_2O_5 lamellar structure is demonstrated not only a significant increase in the conductivity of the composite (up to $10^{-1} \text{ S cm}^{-1}$), but also by the presence of an optical spectrum of the emeraldine form of polyaniline [32]. The participation of oxygen in the oxidation process was proposed assuming that oxygen acts as an electron acceptor [30]. The synthesis of polyaniline with the help of V_2O_5 inside the oxidative host opened up the prospects for obtaining a new class of composites applicable in the field of heterogeneous catalysis and energy-storage devices [33].

Agents with an oxidizing potential below + 1.0 V are also capable for aniline oxidation. They include iron(III) salts [14] (+0.77 V), silver nitrate [14,34] (+0.80 V), compounds of noble metals [35-37] and even copper(II) salts [35] (+0.52 V). However, the formation of a polyaniline-like structure was reliably recorded only for iron(III) ions [14]. Apparently, the reaction proceeds with the participation of oxygen

dissolved in water, with which iron(III) ions form an active complex with a higher oxidation potential [38] or in the combination with hydrogen peroxide (Fenton reagent) [39]. Nevertheless, the content of high-molecular-weight polyconjugated compounds in the reaction products is significantly reduced, and the conductivity is also lower than in the case of peroxydisulfate [14,40]. The products of aniline oxidation with copper(II) and silver(I) salts and other noble-metal compounds [41, 42] may be aniline oligomers or they contain only a fraction of polyaniline. During oxidation, silver and precious metal compounds are reduced to a metallic state, so the product is a metal-organic hybrid [34, 42]. Such hybrids have been used in heterogeneous catalysis, as detection layers for sensors and electrode materials in antibacterial coatings. The synthesis of organometallic hybrids, however, is not without problems. In an acidic environment, the polymerization is very slow and the yield is low.

As for organic oxidants of aniline, oxidative enzymes, peroxidases and laccases, should be mentioned. They are regarded as green chemistry agents for synthesis of polyaniline [43-46]. Enzymes usually include one of the metal ions, such as iron or manganese ion, at redox centers of peroxidases while laccases have copper ones. Enzymes catalyze the exchange of electrons and the formation of the aniline cation radicals. The redox potential for laccase is up to [47] + 0.8 V and redox potential of peroxidases may exceed + 1.0 V [48]. Polyaniline with a conductivity of $10^{-2} \text{ S cm}^{-1}$ was synthesized by using enzymes [49]. Enzymatic catalysis is environmentally benign and its development is important for advances in bioengineering, molecular biology, genetic engineering, etc. At the same time, oxidative enzymes are very sensitive to pH synthesis conditions [48] and have low stability [43]. The synthesis of polyaniline using quinones as oxidants [50] is untenable. It was shown that the reaction of p-benzoquinone with aniline rather yields a trimer-like 2,5-dianilino-p-benzoquinone and not polyaniline [18,51].

Manganese compounds have also been tested as aniline oxidants. Permanganate has the strongest oxidizing power and good solubility in water. The oxidation potential of permanganate in an acidic medium is + 1.69 V. Their use, however, does not lead to the formation of a polyaniline-like structure. In the literature where aniline was oxidized by permanganate and the formation of polyaniline was claimed [52-55] no evidence for the synthesis of polyconjugated structures typical of polyaniline was provided. The products do not have the spectral characteristics of polyaniline [56] and the conductivity was at the level below $10^{-5} \text{ S cm}^{-1}$, which rather corresponds to the conductivity of manganese dioxide, which is formed as a by-product [57]. The synthesis was carried out both in neutral [54] and acidic [55,56] media where, in principle, the formation of aniline oligomers would be possible. The oxidation of aniline with permanganate in media with different acidity thus proceeds rather to quinones.

At the same time, it was demonstrated [58] that manganese dioxide with an oxidation potential of + 1.21 V oxidizes aniline to polyconjugated products with a conductivity of the units of S cm^{-1} . As well as vanadium pentoxide, manganese dioxide is insoluble in aqueous media and heterogeneous synthesis of conducting products proceeds in the optimum pH range in the presence of various organic and inorganic acids. It has also been shown that the oxidative polymerization of aniline is promoted by one-dimensional manganese dioxide nanostructures, while these sacrificial nanotubes disappear and are replaced by polyaniline nanotubes [59]. This transformation could be associated with the oxidative polymerization of aniline on the surface of nanotubes, with the simultaneous reduction of manganese(IV) to a soluble manganese(II) and its removal from the solid reaction products [60].

While the role of manganese dioxide in the synthesis of polyaniline may be regarded as academic, its understanding has a key importance for the preparation of polyaniline/manganese dioxide composites as new materials that are applicable in energy-storage devices, viz. supercapacitors [59-66] and batteries [67], as electromagnetic radiation shielding materials [68], or in sensing devices [69,70]. The present study reports the preparation of such materials and illustrates the original use of composites

as adsorbents of organic dyes, viz. methylene blue and Reactive Black 5, for the application in water-pollution treatment.

2. Experimental

2.1. Preparation

The oxidation of 0.2 M aniline hydrochloride with 0.05-0.5 M manganese dioxide was carried out in 0.5 M hydrochloric acid at room temperature for 24 h. Aniline hydrochloride (2.59 g; p.a., Sigma Aldrich) was dissolved in water to 50 mL solution. Manganese dioxide (2.18 g in stoichiometric experiment; Sigma Aldrich, ~85 wt%, particle size <10 μm) was dispersed under ultrasonic agitation in 50 mL of 1 M hydrochloric acid and added to aniline hydrochloride solution. The reaction mixture was then left for 24 h and occasionally shaken. The solids were separated on a filter, rinsed with ethanol, and dried in open air. The reference polyaniline was prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in water [11].

2.2. Characterization

Morphology was assessed with a Tescan MAIA2 ultra-high-resolution scanning microscope. The conductivity was determined by a four-point van der Pauw method using pellets 13 mm in diameter and ≈ 1 mm thick prepared from powders by compression with a manual hydraulic press at 527 MPa. The setup included a Keithley 2010 multimeter, a Keithley 220 current source and a Keithley 705 scanner. FTIR spectra were recorded using Nicolet 6700 (Thermo-Nicolet, USA) spectrometer equipped with a reflective ATR extension GladiATR (PIKE Technologies, USA) with diamond crystal and a deuterated L-alanine doped triglycine sulfate detector at 4 cm^{-1} resolution with 64 scans. X-ray diffraction (XRD) patterns were obtained using a HZG-4A powder diffractometer (Seifert GmbH, Germany). The radiation CuK α wavelength 0.154 nm mono-chromatized with Ni foil was used. The measurement was done in the angular range 1.4°-50° with 0.18° steps.

The dye adsorption was tested with Reactive Black 5 (Sigma-Aldrich, > 50 wt% dye content) and methylene blue (Sigma-Aldrich; for biological staining) which were used as delivered without any correction for true dye content. The mass adsorbent/dye ratio was 10. The 50 mL of dye solution in water (100 mg L^{-1}) was poured over 50 mg of material tested as an adsorbent, and the peak optical absorbance at 598 nm for Reactive Black 5 and 664 nm for methylene blue was recorded at various times with a Perkin-Elmer Lambda 20 UV-vis spectrometer.

3. Results and discussion

3.1. Preparation

Polyaniline is prepared by the oxidation of aniline in acidic aqueous medium. A typical oxidant, ammonium peroxydisulfate, yields two electrons and the oxidant-to-aniline mole ratio has to be 1.25 in order to obtain polyaniline salt in emeraldine oxidation state [11] (**Fig. 1**). The same ratio is expected for another oxidant, manganese dioxide (**Fig. 2**). Aniline was oxidized at various MnO_2 concentrations and the oxidant-to-aniline mole ratio ranged from 0.25 to 2.5, which was both lower and higher than the stoichiometric one. The yield of the product, its qualitative and quantitative composition and conductivity were determined (**Table 1**).

3.2. There are three differences between both oxidants

(1) Insolubility of manganese dioxide in water or in the solution of acids makes the substantial difference to ammonium peroxydisulfate, which is well soluble. The oxidation of aniline hydrochloride thus has heterogeneous character, yet it proceeds easily. This is due to the reductive dissolution of solid transition-metal oxides in the presence of reducing species [71-74], such as, in the present case, aniline. Please note that such dissolution need not occur at the site where the reductant adsorbs at the solid (Fig. 3).

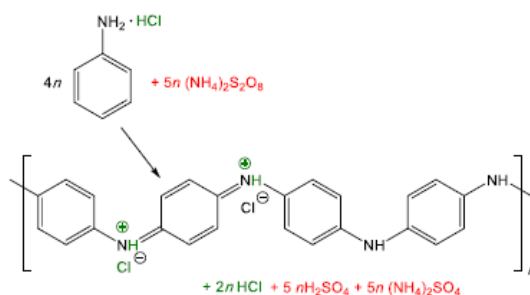


Fig. 1. Preparation of polyaniline hydrochloride by the oxidation of aniline hydrochloride with ammonium peroxydisulfate.

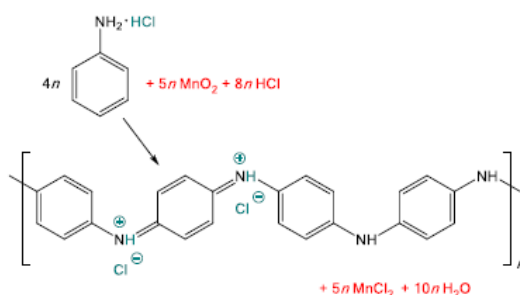


Fig. 2. Preparation of polyaniline hydrochloride by the oxidation of aniline hydrochloride with manganese dioxide.

Table 1 The oxidation of aniline hydrochloride with solid manganese dioxide: Yield, Y, per gram of a monomer, conductivity, σ , and sample composition.

$[\text{MnO}_2]/[\text{aniline}]$	Y, g g ⁻¹ ,	σ , S cm ⁻¹	Mn ⁴⁺ , wt%	MnO ₂ ^b , wt%
0.25	0.162	1.86	—	—
0.5	0.297	1.76	0.17	<0.1
0.75	0.448	2.26	—	—
1	0.699	3.58	—	—
1.25 ^c	0.811	2.86	0.95	0.9
1.5	0.973	2.34	—	—
2	1.093	0.0807	—	—
2.5	1.340	0.00688	33.3	21.9

^a Estimated from EDAX.

^b Determined as an ash.

^c Stoichiometric composition (cf. Fig. 2).

Instead, the electrons can travel from the reductant through the oxide particle, be accepted by the oxidant, thus causing its dissolution elsewhere on the particle. Some level of the conductivity of the

oxide is required; for the manganese dioxide of various types it is of the order 10^{-3} - 10 S cm^{-1} [75]. The analogous redox process, when the transfer of electrons from the reductant to the oxidant does not take place by the direct contact of interacting molecules but through a conducting material, polyaniline, had also been proposed to explain the polymerization of aniline in the solid state [76], in the frozen aqueous media [77,78], or the role of conducting polymers in the corrosion of metals [79], where the diffusion of reactants is highly restricted.

(2) Oxidation potential E of manganese dioxide is lower compared with peroxydisulfate. It is still sufficient for the oxidation of aniline under acidic condition, because at increased acidity, the oxidation potential of MnO_2 is above the critical limit required to initiate the growth of regular polymer chains [80] (1.05 V vs NHE).

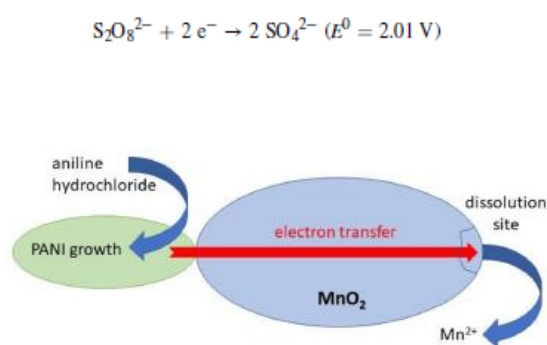


Fig. 3. Reductive dissolution of manganese dioxide during oxidative polymerization of aniline hydrochloride to polyaniline.



(3) Acidity conditions have to be considered. Only the oxidation of aniline at $\text{pH} \leq 2.5$ yields conducting polyaniline, while the oxidation at higher pH results in the formation of non-conducting aniline oligomers [17,81]. The oxidation of aniline hydrochloride with MnO_2 was also carried out at the 0.25-2.5 oxidant-to-aniline mole ratio in the absence of added acid (initial pH 2.8). Only brown oligomers and their composites with MnO_2 were obtained. Their conductivity was below 10^{-6} S cm^{-1} , i.e. they were regarded as non-conducting from the practical point of view. For that reason, they have not been further investigated. Under similar conditions the synthesis of polyaniline using peroxydisulfate leads to opposite results: here, conducting polyaniline with a conductivity of units S cm^{-1} is produced in a high yield. The difference between the two oxidative reactions is that sulfuric acid is a by-product of per-oxydisulfate reduction [16] (Fig. 1) and, as a result, during the synthesis the initial pH 2.8 drops below 1. In contrast, the by-product of MnO_2 reduction is water and acid is consumed in this reaction (Fig. 2), which leads to a decrease in acidity from pH 2.8 to pH 4.

3.3. Yield

At fixed concentration of aniline, the theoretical yield of polyaniline should increase in direct proportionality to the concentration of oxidant up to the stoichiometric ratio of both reactants (Fig. 4). When using insoluble oxidant, such as manganese dioxide, its presence can contribute to the yield, which is determined as solids after the completion of reaction. The fact that the experimental yield follows the theory means that manganese dioxide was completely converted to soluble manganese(II) salts and the product is thus represented by polyaniline only.

When using the oxidant in excess of stoichiometric ratio, the unreacted insoluble oxidant could contribute to the yield and a poly-aniline/manganese dioxide composite could be produced instead of polyaniline only (**Fig. 3**). The experimental data, however, clearly demonstrate the negative deviation, i.e. the yield lower than expected for a simple composite formation. This means that a part of manganese dioxide was still used to oxidize emeraldine form of polyaniline to pernigraniline [82] and converted to a soluble manganese(II) salt. Per-nigraniline itself has limited stability and may decompose at the same time to yield soluble p-benzoquinone [83]. Both processes thus reduce the reaction yield compared to the theoretical prediction. Thus, based on the analysis of the yield of synthesis products, it is assumed that a neat polyaniline is produced at oxidant-to-aniline mole ratio ≤ 1.25 and, in the case of an excess of manganese dioxide, the product becomes a composite of polyaniline and manganese dioxide, which contains polyaniline in overoxidized pernigraniline form.

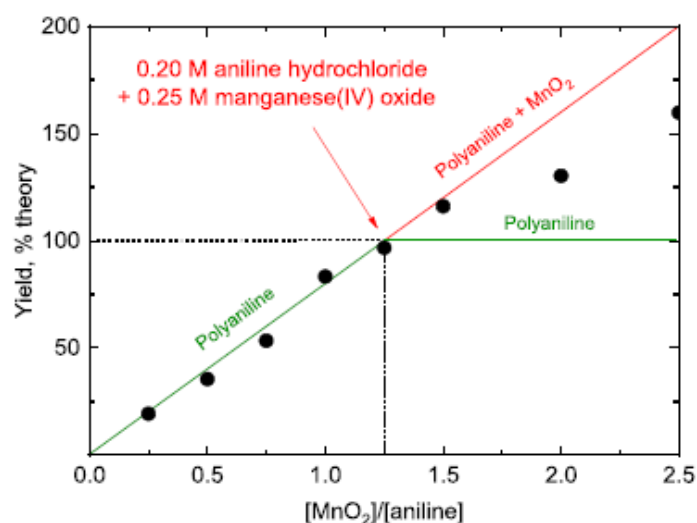


Fig. 4. The expected (lines) and obtained yield (full circles) relative to the stoichiometric expectation (defined by dashed lines and arrow) for the oxidation of 0.2 M aniline hydrochloride with various molar concentrations of manganese dioxide (**Fig. 2**).

3.4. Morphology

Manganese dioxide consists of amorphous polydisperse particles from tens of micrometers to submicrometer sizes (**Fig. 5**). After interaction with aniline, regardless of the oxidant-to-aniline mole ratio, the general view of the morphology does not change, i.e. the final product reproduces the structure of the oxidant at submicrometer level. This suggests that polymer chains grow as a layer at the surface of MnO₂ particles. Aniline is oxidized to polyaniline and reduces manganese dioxide to soluble manganese(II) chloride (**Fig. 2**), while polyaniline replaces the oxidant by reproducing the shape of its particles (**Fig. 3**). It is expected that polyaniline encapsulates unreacted MnO₂ in composite materials. Indeed, during the oxidation of aniline using one-dimensional MnO₂ particles, MnO₂ nanotubes were transformed to polyaniline nanotubes [59]. The image of polyaniline obtained at stoichiometric oxidant-to-aniline mole ratio, where according to the analysis MnO₂ is absent, demonstrates that the general appearance of the structure coincides with that of initial MnO₂.

During synthesis, the polyaniline chains are also self-assembled and the type of morphology at the submicrometer and nano-level depends on the synthesis conditions [12]. It should be noted that the structure of polyaniline particles obtained by the oxidation with MnO₂ differs from that obtained under the same experimental conditions with peroxydisulfate (**Fig. 5**). A tendency of one-dimensional growth is observed with MnO₂, in contrast to spherical particles characteristic of peroxydisulfate

oxidation [81]. This is attributed to the lower oxidation potential of MnO₂ compared to peroxydisulfate [13].

3.5. Composition

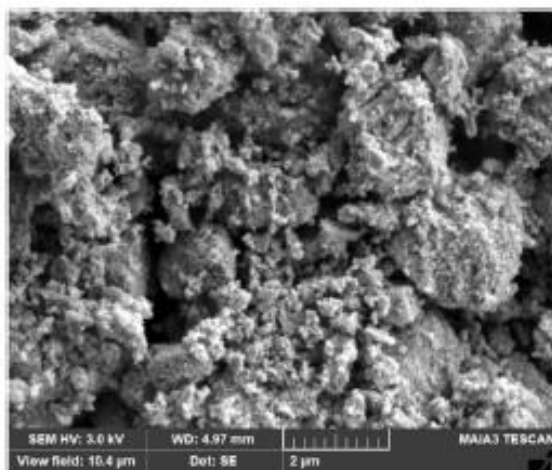
The EDAX provides the qualitative proof of the absence of manganese in the samples prepared at and below stoichiometric ratio [MnO₂]/[aniline] ≤ 1.25, and its presence in the sample prepared at oxidant excess (Table 1, Fig. 6). The latter result is, however, affected by the use of carbon tape and platinum used in the sample preparation for microscopy. The direct determination of MnO₂ content as an ash is more convincing (Table 1). It should be noted that the EDAX analysis provides the surface composition and is therefore not suitable for determining the total amount of manganese in the entire sample volume.

3.6. X-ray diffraction

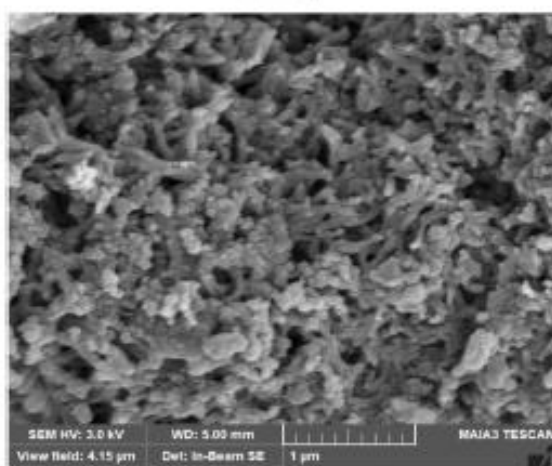
Diffraction patterns of the samples obtained at an oxidant-to-aniline mole ratio ≤ 1.25 with MnO₂ content below 1 wt% demonstrate only the characteristics of the conducting form of amorphous polyaniline [84-86], i.e. amorphous halo on which two broad peaks appear at 2θ = 22° (3.5 Å; periodicity along polymer chains) and 260 (4.4 Å; periodicity across polymer chains) (Fig. 7). In the samples obtained at a high content of the oxidant, the presence of MnO₂ is observed. The diffractogram of weakly crystalline MnO₂ exhibits broad peaks of pyrolusite structure at 2θ = 28°, 37°, and 43° based on MnO₆ octahedra building blocks which produce one-dimensional channel structure with cell parameters 4.38 Å and 2.85 Å [87,88]. These peaks are traced without displacement in the diffraction patterns of the sample containing 21.9 wt% MnO₂ obtained at an oxidant-to-aniline mole ratio ≥ 1.25.

3.7. FTIR spektra

The ATR FTIR spectroscopy is convenient technique to study the molecular structure of the polymer chains growing as layers at the surface of manganese dioxide particles (Fig. 5). The spectra of the samples produced at oxidant-to-aniline mole ratio ≤ 1.25 (Fig. 8) are close to the spectrum of “standard” polyaniline [1] (spectrum PANI in Fig. 8).



MnO_2



Polyaniline prepared with MnO_2

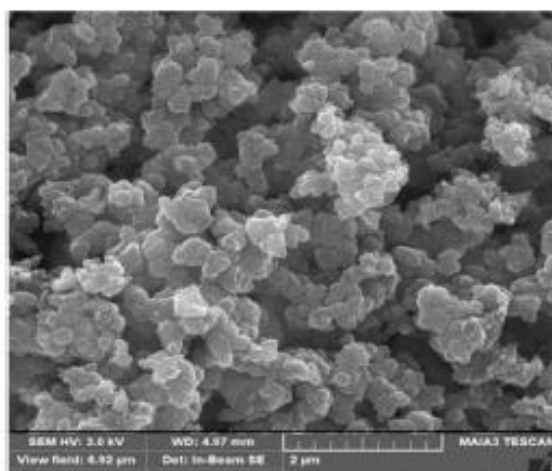


Fig. 5. Scanning electron micrographs of manganese dioxide, polyaniline prepared at stoichiometric mole ratio $[\text{MnO}_2]/[\text{aniline}] = 1.25$ and of reference polyaniline with ammonium peroxydisulfate.

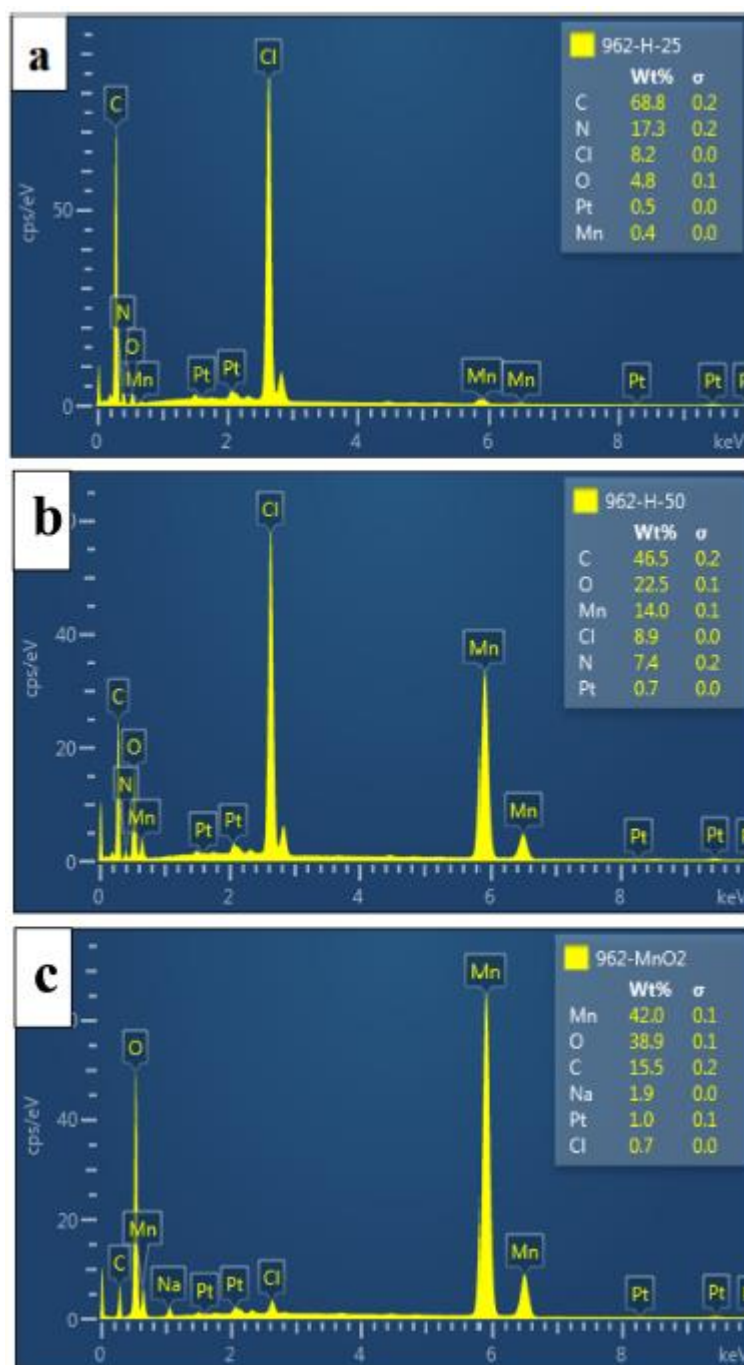


Fig. 6. EDAX elemental analysis of (a) polyaniline prepared at stoichiometric mole ratio $[\text{MnO}_2]/[\text{aniline}] = 1.25$, and (b) the composite at oxidant excess, $[\text{MnO}_2]/[\text{aniline}] = 2.5$, compared with (c) the pattern of neat MnO_2 .

They are in protonated state with relatively high conductivity (**Table 1**). In the case of an excess of manganese dioxide, the spectra dramatically change and they are close to the spectra of polyaniline base, i.e. with larger proportion of quinonedimine units than in a common polyaniline prepared with peroxydisulfate. It may correspond to the presence of polyaniline in form of pernigraniline base. The conductivity of these samples dramatically decreased (**Table 1**). These are expected polyaniline/ MnO_2 composites, but the presence of manganese dioxide does not manifest itself in the spectra.

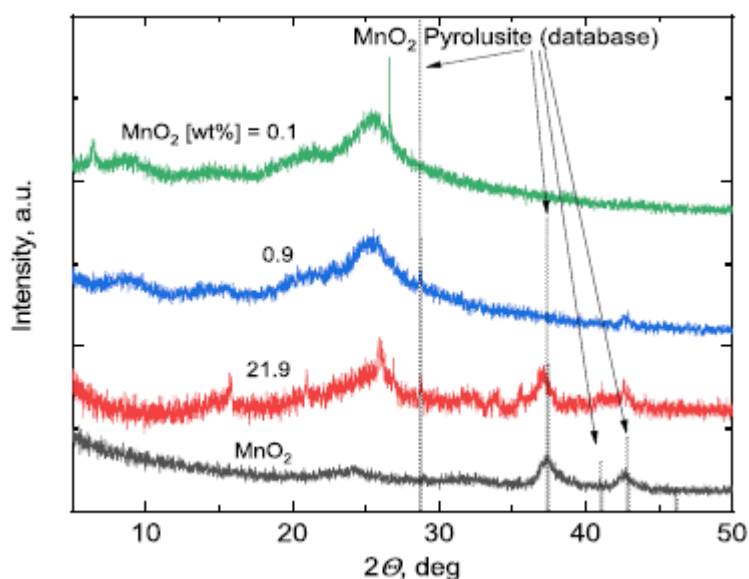


Fig. 7. X-ray diffractograms of polyaniline prepared with MnO_2 and polyani-line/ MnO_2 .

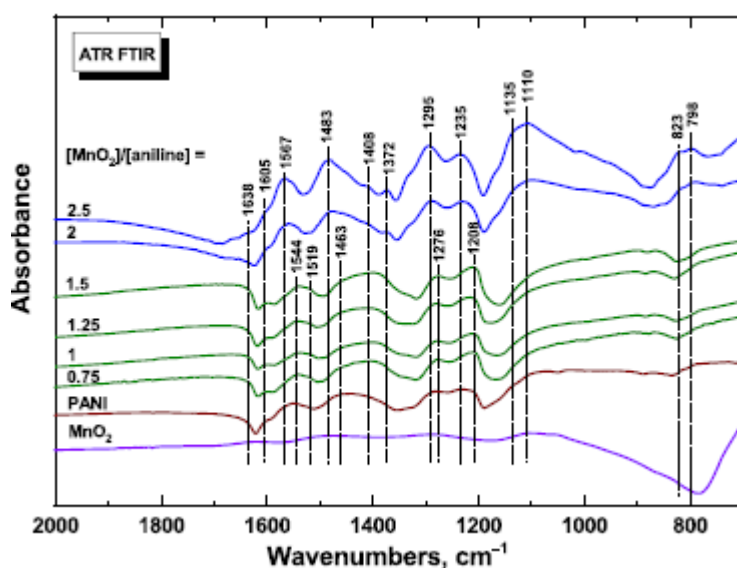


Fig. 8. ATR FTIR spectra of the oxidation products of aniline prepared at various $[\text{MnO}_2]/[\text{aniline}]$ ratios. The spectrum of “standard” polyaniline (PANI) is shown for comparison.

3.8. UV-vis spectra

The formation of polyaniline, a polymer with a regular structure of monomer units providing conjugation is confirmed by the UV-vis spectra (Fig. 9). In the visible range, polyaniline is characterized by two types of bands: (1) the π - π^* band of electronic transitions in benzenoid and quinonoid rings (~ 300 nm region) and (2) a wide excitation band of charge carriers, polarons, above 800 nm [89-91]. In the deprotonated non-conducting state, a significant shift of the band to the 600 nm region is observed (Fig. 9). The Fig. 9 compares the spectra of dedoped polyaniline obtained using peroxydisulfate and manganese dioxide oxidants. The spectra are nearly identical, however, the use

of an excess of latter oxidant leads to a slight hypsochromic shift of the absorption band from 610 nm to 588 nm. This is explained by the partial overoxidation of polyaniline in the presence of manganese dioxide.

3.9. Conductivity

The conductivity of polyaniline prepared at 0.05-0.3 M MnO_2 was virtually independent of the oxidant concentration and varied between 1.86 and 3.58 S cm^{-1} (**Fig. 10**). The conductivity of 2.86 S cm^{-1} at stoichiometric composition is consistent with the conductivity of "standard" polyaniline repeatedly prepared with peroxydisulfate oxidant $4.37 \pm 1.74 \text{ S cm}^{-1}$ [1,11].

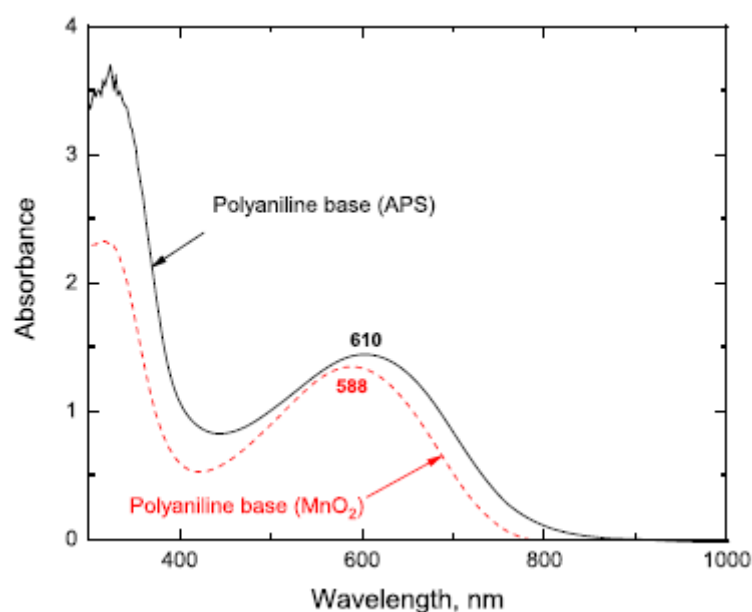


Fig. 9. The UV-vis spectrum of polyaniline base prepared with ammonium peroxydisulfate (full line) and manganese dioxide (broken line) at stoichiometric conditions and dissolved in N-methylpyrrolidone.

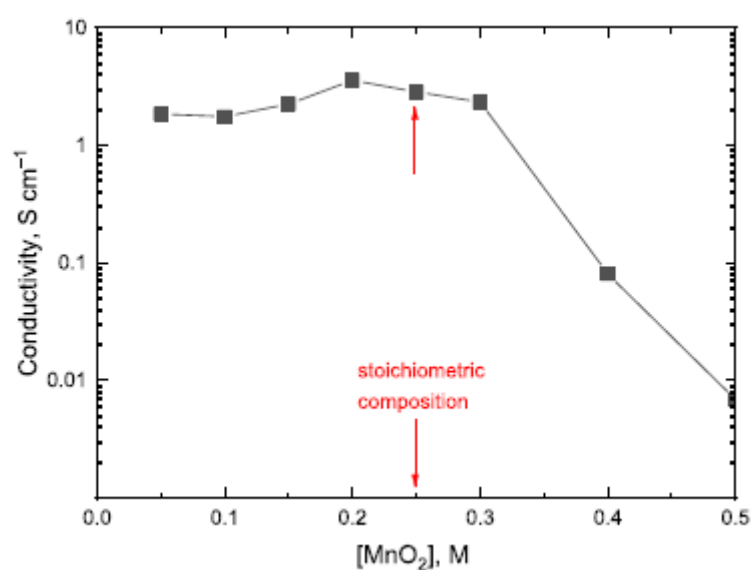


Fig. 10. Conductivity of the oxidation product of 0.2 M aniline hydrochloride with various molar concentrations of manganese dioxide. For stoichiometric reaction, mole ratio $[\text{MnO}_2]/[\text{aniline}] = 1.25$ (cf. **Fig. 2**).

At higher oxidant concentration, 0.4-0.5 M MnO_2 , the conductivity of the product is reduced due to the overoxidation of emeraldine form of polyaniline to pernigraniline and incorporation of less conducting manganese dioxide (**Fig. 10**).

3.10. Dye adsorption on polyaniline

The adsorption of organic dyes at conducting polymers is one of the prospective application fields in water-pollution treatment [9] that is not related to electrical properties [2]. This phenomenon is based on n-n interactions between conjugated molecular structure that both moieties share, in the combination with hydrogen bonding, electrostatic interactions and van der Waals forces [92]. This was illustrated in the literature also on the adsorption of anionic azo dye, Reactive Black 5 at polyaniline [93] and its composites [94]. Indeed, when in the present case polyaniline was added to the dye solution, the optical absorbance decreased until virtually all dye had been consumed. Only grey background caused by absorption of small dispersed polyaniline particles was left (**Figs. 11, 12**). By comparing the time dependence of the optical absorbance at the maximum at 598 nm for polyaniline prepared with manganese dioxide and ammonium peroxydisulfate at the stoichiometric oxidant-to-monomer mole ratio, we observe that both polyanilines behave in the same manner and can be regarded in this respect as identical (**Fig. 13**).

Similar dependence was also determined for cationic thiazine dye, methylene blue. In this case, polyaniline prepared with manganese dioxide performed slightly better (**Fig. 13**), but still the adsorption was lower compared to Reactive Black 5. Polyaniline is a polycation (**Fig. 2**). It is tempting to speculate that anionic dyes are better attracted to this polymer than the cationic ones. The prevailing opinion expressed in the literature, however, is that electrostatic interactions do not dominate in the dye adsorption [9].

3.11. Dye adsorption on polyaniline/ MnO_2 composite

The dye adsorption on polyaniline prepared with manganese dioxide (MnO_2 <1 wt%) and polyaniline/manganese dioxide composite (MnO_2 = 21.9 wt%) reveals the better adsorption by polyaniline alone (**Fig. 14**). This means that polyaniline is the adsorbent controlling the overall dye adsorption. The better accessibility of polyaniline shell to the dye adsorption in core-shell structure with manganese dioxide core contributes to this behavior. It should be noted that manganese dioxide alone was reported as an adsorbent of crystal violet, methylene blue [95] or Reactive Orange 13 [96]. We can confirm that, for example, methylene blue can be indeed adsorbed by manganese dioxide but on considerably longer time scale compared with polyaniline.

4. Conclusions

Solid manganese dioxide is insoluble in the acidic aqueous solutions, yet it is able to oxidize aniline to polyaniline at the simultaneous reductive dissolution. The stoichiometric oxidant-to-monomer mole ratio $[\text{MnO}_2]/[\text{aniline}] = 1.25$ was confirmed by the reaction yield and analysis of products. A higher initial acidity of the reaction medium is required to obtain conducting polyaniline when using MnO_2 instead of peroxydisulfate. While in the oxidation with peroxydisulfate the protons are generated, with MnO_2 oxidant they are consumed. Polyaniline obtained under the action of MnO_2 in general reproduces the morphology of the solid oxidant and at the nanoscale there is a tendency to form one-

dimensional morphologies. In addition, UV-vis and FTIR spectroscopies revealed the higher oxidation state in polyaniline prepared with excess of manganese dioxide.

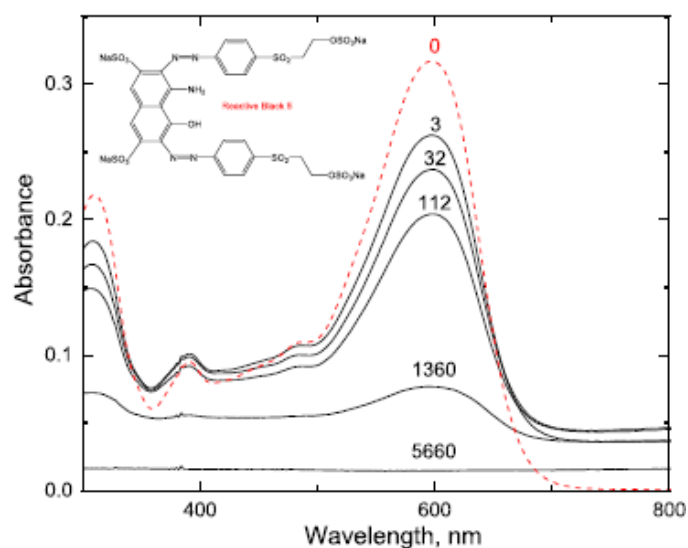


Fig. 11. UV-vis spectra of the aqueous solution of Reactive Black 5 (100 mg L⁻¹) recorded at various times (min) after addition of polyaniline (1 g L⁻¹). The original spectrum of dye solution is depicted by dashed line.



Fig. 12. The solution of Reactive Blue 5 (left) and its decolorization with polyaniline after ca 5 days. The conditions as in Fig. 12.

Polyaniline is exclusively produced below stoichiometric ratio, $[\text{MnO}_2]/[\text{aniline}] < 1.25$, and does not contain any manganese dioxide due to its dissolution. Such polyanilines have the conductivity of the order of units S cm^{-1} , i.e. the same as polyanilines prepared with standard oxidation with ammonium peroxydisulfate. Both oxidants produce polyanilines, which act as identical adsorbents of an organic dye, Reactive Black 5, and less efficient but also similar adsorbents of methylene blue.

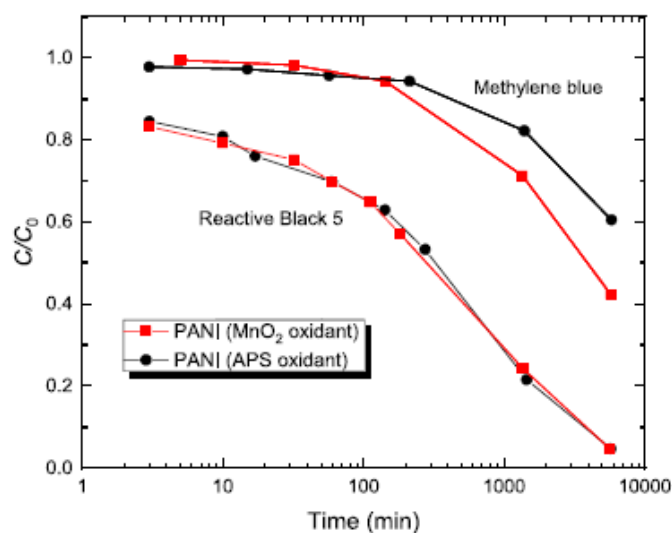


Fig. 13. Time dependence of the relative decrease in dye concentration, C/C_0 , for polyaniline prepared with manganese dioxide or with ammonium peroxydisulfate for solutions of anionic Reactive Black 5 and cationic methylene blue. The conditions as in Fig. 11.

Only when excess oxidant was used, $[MnO_2]/[aniline] > 1.25-2.5$, the polyaniline/manganese dioxide composites are produced. The results offer the route how to prepare such composites for various applications, e.g. in water-pollution treatment. They also provide understanding of the processes that may take place in the coating of solid manganese dioxide by routine in-situ polymerization of aniline with ammonium peroxydisulfate, which has often been used in the literature for energy-storage devices.

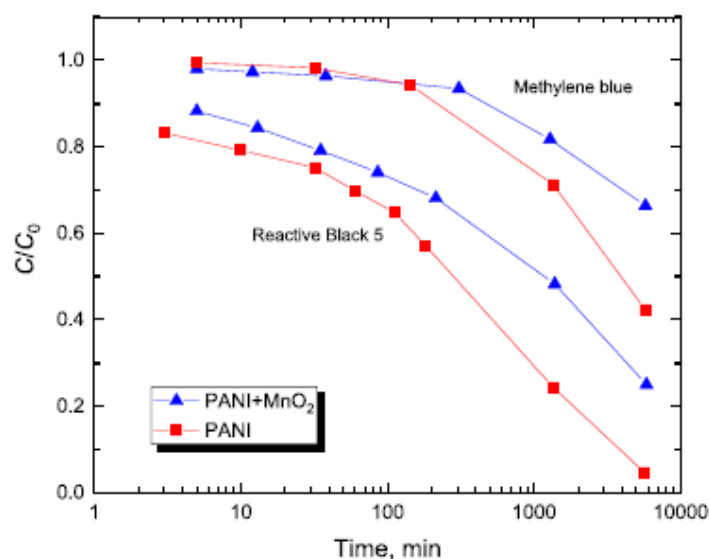


Fig. 14. Time dependence of the relative decrease in dye concentration, C/C_0 , for polyaniline prepared with manganese dioxide and polyaniline/manganese dioxide composite for solutions of anionic Reactive Black 5 and cationic methylene blue. The conditions as in Fig. 11.

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