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Chapter

Polyaniline-Based Nanocomposites for Environmental Remediation

Thabiso C. Maponya, Mpitloane J. Hato, Thabang R. Somo,
Kabelo E. Ramohlola, Mogwasha D. Makhafola,
Gobeng R. Monama, Arjun Maity, Kwena D. Modibane
and Lebogang M. Katata-Seru

Abstract

With growth in civilisation and industrialisation, there is an increase in the release of toxic heavy metal ions and dyes into water system, which is of public concern. As a result, appropriate treatment methods have to be implemented in order to mitigate and prevent water pollution. The discovery of nanotechnology has led to the development and utilisation of various nanoadsorbent for the removal of pollutants from water. PANI nanostructures and nanocomposites are noble adsorbents that have gained popularity in addressing water pollution issues and have been reported in literature. In this chapter, the main focus is on the synthesis of PANI nanocomposites and nanostructures and their application as efficient adsorbents for water treatment. Detailed discussions on different synthetic routes and characterisation have been dedicated to applications of these materials and are compared for the adsorptive removal of heavy metal ions and dyes from water.

Keywords: conducting polymers, polyaniline, composites, water remediation

1. Introduction

The existence of various toxic pollutants in natural water systems originating from different activities such as textile industry, mining operation and steel manufacturing is still a global challenge [1]. Hence, it is vital to develop efficient technologies to remove these pollutants from wastewater prior release into the environment. Among several water treatment processes (coagulation, membrane filtration, chemical reduction and precipitation, reverse osmosis), adsorption technology is deemed an efficient technology to treat wastewater due to exceptional advantages such as low cost, high removal efficiency and regeneration [1]. For many years, there has been an ongoing research on the development of high affinity materials towards water pollutants, which can effectively adsorb and remove them from industrial wastewater [2]. Conducting polymers (CPs) including polypyrrole (PPy), polythiophene (PTh), polyacetylene (PA) and polyaniline (PANI) have attained great attention for water treatment, owing to their intriguing properties such as ease synthesis, tunable structure and the presence of ideal functional groups [3]. Hence, CPs have been widely applied in materials such as rechargeable batteries, chemical sensors, electrochromic devices, surface coating for corrosion protection and water treatment [4]. Among

these conducting polymers, PANI has been widely studied due to its low cost, ease of synthesis, good environmental stability, unique doping/de-doping property and relatively high conductivity [5]. The discovery of PANI dates back to about 180 years ago to the experiments made by Runge [6]. From his work reported in 1834, he discovered that a dark green PANI changed to black when the mixture of copper(II) chloride and aniline nitrate is heated on a porcelain plate to 100°C [6, 7]. Anciently, PANI was known as 'aniline black', after forming an undesirable black powder deposit on the anode during oxidation of aniline [8, 9] and is the most stable CP that can be easily protonated (with an acid) to increase conductivity or deprotonated (with a base) to reduce its conductivity [10]. In 1862, Letheby prepared it through oxidation of aniline under mild conditions [9, 11]. Attempt to control the synthesis conditions of polyaniline grew until in the 1910s when Green and Woodhead managed successfully to control the conditions, which led to the discovery of its four oxidation states [8]. This was followed by Jozefowic's group in the 1960s and 1970s for better understanding of the material [6, 8]. After this, the study of polyaniline with other (intrinsic conducting polymers) ICPs increased tremendously worldwide and were studied for different applications.

2. Synthesis of polyanilines

Polyaniline have different chemical structures which is attributed to the oxidation state of the polymer backbone, hence it exists in different states [12, 13]. The general representation of the polyaniline structure can be described by the following structural formula (**Figure 1**):

were y = 1, 0.5 and 0 correspond to fully reduced polyaniline (leucoemeraldine), the half oxidised polyaniline (emeraldine) and fully oxidised polyaniline (pernigraniline), respectively [13]. Upon doping, PANI can be interconverted from one oxidation state to another [13]. The interconversions can be clearly deduced as presented in **Scheme 1**.

There are two general methods which are employed to synthesise conducting polymers through electrochemical oxidation of the monomers or chemical oxidation of the monomers, namely: electrochemical polymerisation and chemical polymerisation.

2.1 Electrochemical polymerisation

Electrochemical polymerisation or method can be carried out by employing one of the three techniques: (i) applying a constant current (galvanostatic), or (ii) applying a constant potential (potentiostatic), and lastly (iii) by applying a potential scanning/cycling to the aqueous solution of aniline [14]. Polymerisation process is performed in strongly acidic aqueous electrolyte using a radical polymerisation mechanism which allows a formation of anilinium radical cation
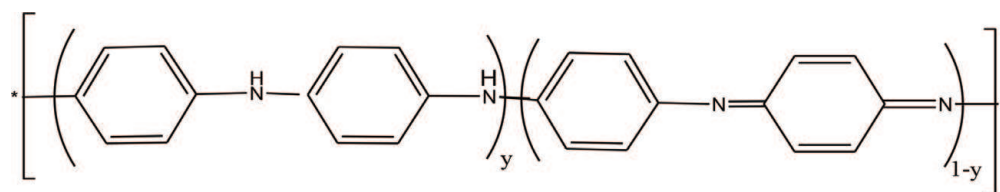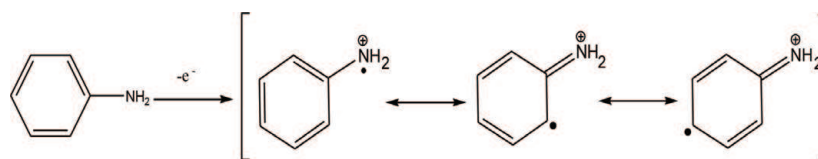

Figure 1.
The general structure of polyaniline.

Scheme 1.
Oxidation of aniline monomer during polymerisation of aniline [21, 22].

by aniline oxidation on the electrode[15, 16]. Electrochemical polymerisation strongly depends on the following factors:

a. low pH which is needed for preparation of conductive polymeric materials,

b. the dopant anion incorporated into polymer to determine the morphology, conductivity, rate of polymerisation growth and influences degradation process and

c. inert electrode such as Pt, Au and graphite [17].

The electrochemical process is more advantageous since film properties such as thickness and conductivity can be controlled by the synthesis parameters, including the current density, substrate, pH, nature and concentration of electrolyte [18].

2.2 Chemical polymerisation

Like electrochemical polymerisation, chemical polymerisation is also carried out in an acidic medium such as hydrochloric acid (HCl) and formic acid which helps in yielding primary polymer [19]. For this process to occur, a dopant or oxidant is required. The dopant reagents used during this process are the oxidising agents such as ammonium persulfate (APS), ferric chloride ($FeCl_3$), hydrogen peroxide (H_2O_2) and ceric nitrate ($Ce(NO_3)_3$). The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong coordination bond either with the substrate intermediate or with the final product [20].

The general mechanism involved during polymerisation of aniline proceeds dominantly via radical mechanisms. Radical mechanisms can be subdivided into initiation, chain propagation and termination steps, which results in stable intermediate resonance structures. The three different stages of polymerisation are illustrated from **Scheme 1–3**.

### 2.2.1 Step 1: initiation step (oxidation of aniline monomer)

The initial step of aniline oxidative polymerisation is the generation of the aniline cation radical in the oxidation of aniline with an oxidant as shown in **Scheme 1** [21, 22]. The aniline cation radical undergoes resonance to attain the most stable and reactive radical cation which is free from steric hindrances [23]. This step is the slowest step in the reaction, hence it's deemed as the rate determining step in aniline polymerisation [24].

2.2.2 Step 2: radical coupling and re-aromatisation

Head to tail coupling of the *N*- and *para*- radical cations takes place (**Scheme 2**), yielding a dicationic dimer species. This dimer further undergoes the process of re-aromatisation which causes it to revert to its neutral state, yielding an
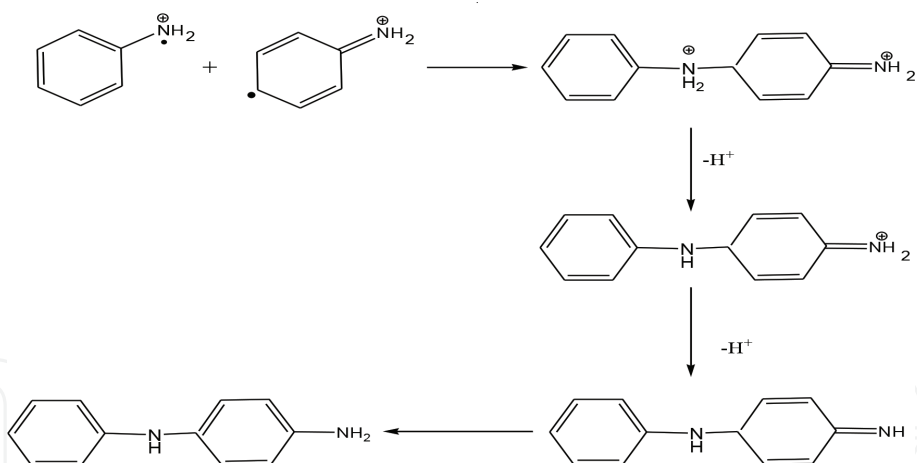
Scheme 2.
Formation of a dimer [25, 27].
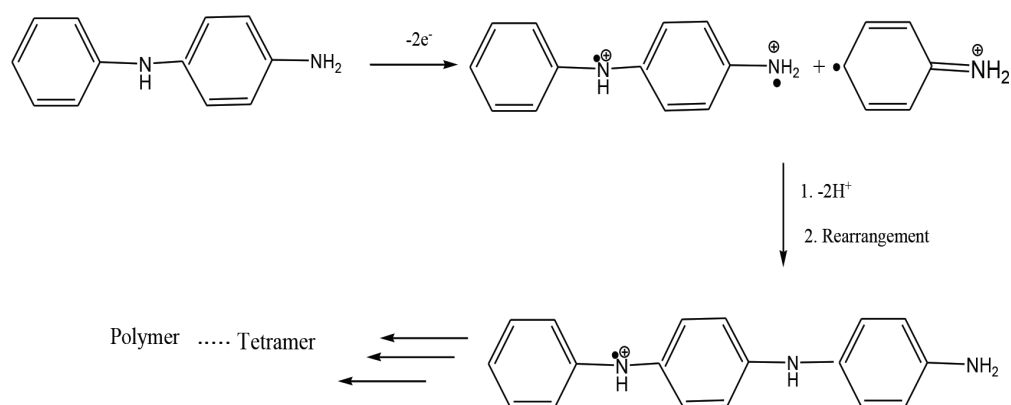
Scheme 3.
Formation of a trimer and polymer formation [27].

intermediate referred to as *p*-aminodiphenylamine (PADPA) [25, 26]. These processes are also accompanied by the elimination of two protons.

2.2.3 Step 3: chain propagation

The dimers are immediately oxidised and then react with a stable aniline cation radical via an electrophilic aromatic substitution, followed by deprotonation and rearrangements to afford the trimer as seen in **Scheme 3** [27]. The trimer further undergoes oxidation and reacts with aniline cation radical to form a tetramer and so on.

3. Synthesis and characterisation of polyaniline nanocomposites

Different nanocomposites based on polyaniline have been reported for wastewater remediation in order to enhance the removal efficiency of polyaniline. Depending on the method of synthesis, a variety of PANI based nanostructures and nanocomposites can be developed. For example, Ren et al. [28] reported PANI/PAN (polyacrylonitrile) nanocomposite synthesised via in–situ polymerisation of ANI monomer using DBSA and APS to obtain a nanofibrous structures as depicted in **Figure 2a**. Rachna and co-workers [29] reported zinc ferrite-PANI nanocomposite prepared following similar preparation method and monomer using toluene as a solvent and $CuSO_4$. The SEM image (**Figure 2b**) showed that the nanocomposite
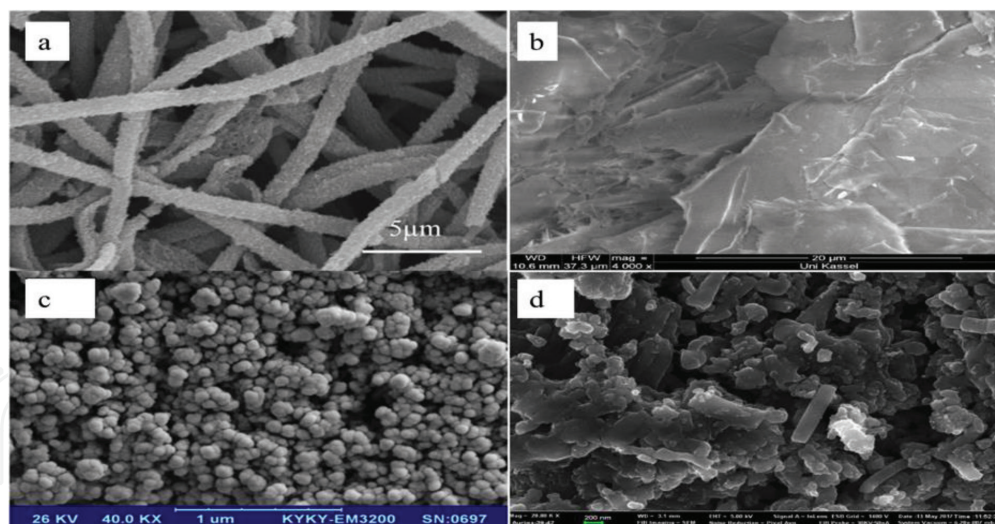
Figure 2.
SEM images of different structures of PANI nanocomposites (a) fibres [28], (b) smooth surface [29], (c) spherical [30] and (d) tubular [2].

had a smooth surface. Tanzifi et al. [30] prepared PANI/carboxymethyl cellulose/ titanium dioxide PANI/CMC/TiO$_2$ nanocomposite in acidic medium using the same polymerisation route and APS as an oxidising agent. The nanocomposite structure formed uniform spherical particles as indicated in **Figure 2c**. PANI@Ni(OH)$_2$ nanocomposite was prepared by Bhaumik et al. [2] via in–situ polymerisation using APS and hydrazine hydrate. The SEM image showed a tubular structure as represented in **Figure 2d**.

Hallajiqomi et al. [31] synthesised PANI/PVP nanocomposite via in–situ polymerisation using KIO$_3$ and PVP as oxidising agent and surfactant, respectively. The nanocomposite showed irregular structural morphology. PANI/reduced graphene oxide (RGO) nanocomposite was synthesised by Li et al. [32] following the same polymerisation route using APS as an oxidising agent. The nanocomposite exhibited a lamellar structure. In another study, Harijan and Chandra [33] reported a PANI-GO nanocomposite synthesised by similar preparation method and the nanocomposite was composed of sheet-like morphology. Wang et al. [34] synthesised PANI/α-ZrP with plate–like structures via in–situ polymerisation using the same oxidising agent. In another study, Abdolahi et al. [35] synthesised uniform PANI nanofibers through interfacial polymerisation with different sizes ranging from micro- to nanometers. Gold-polyaniline (AuPANI) nanocomposite was prepared by simple interfacial polymerisation, performed in an immiscible water/ toluene biphasic system using tetrachloroaurate, as an oxidant [36]. The TEM images of AuPANI nanocomposite showed rod-like Au nanoparticles embedded in a PANI matrix (see **Figure 3a-d**). Dhachanamoorthi et al. [37] prepared PANI-iron oxide (Fe$_3$O$_4$) ternary nanocomposites with improved crystallinity upon addition of Fe$_3$O$_4$ by mechanical mixing approach. Similar method was used for the synthesis of PANI-zinc oxide (ZnO) nanocomposites with enhanced electrical conductivity and homogeneous distribution on ZnO nanoparticles in the polymer matrix [38]. Basavaiah et al. [39] prepared polyaniline nanorods and magnetite nanoparticles via self-assembly route.

Table 1 shows some of the PANI based nanocomposites reported for the removal of pollutants from wastewater. The most commonly used method is the in–situ chemical polymerisation, which can result in various morphological structures. The structure of the nanocomposite is strongly affected by the type of oxidant, surfactant or stabiliser, the precursor and the ratio of the precursor to that of ANI.
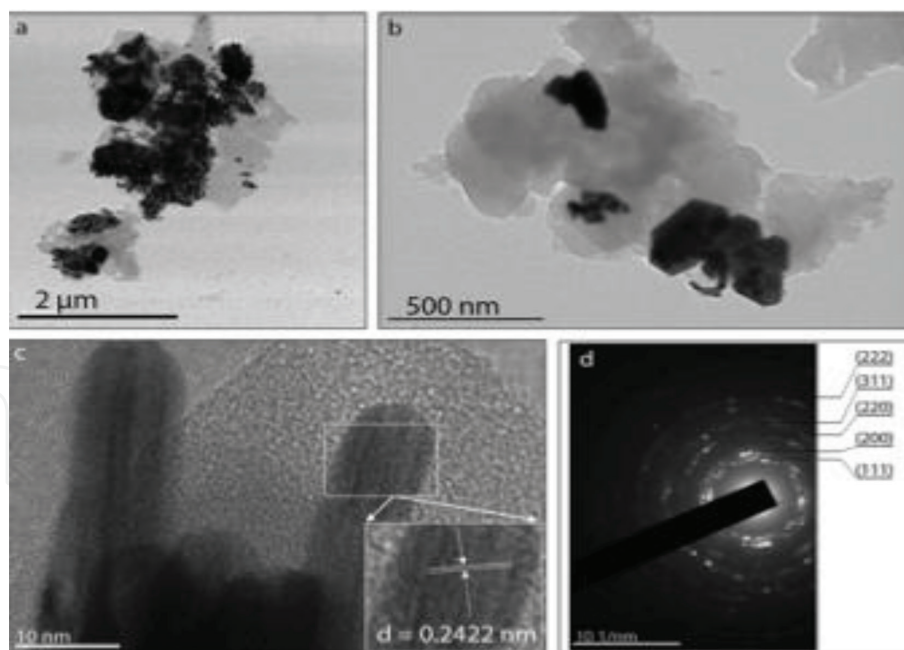
Figure 3.
TEM images of AuPANI nanocomposite with different magnifications (a, b, c) showing rod-like Au nanoparticles embedded in a PANI synthesised by interfacial polymerisation and (d) corresponding selected area electron diffraction (SAED) [36].

Adsorbent	Synthesis method, oxidant and/or other reagents	Morphology	Refs.
PANI-PPy	a, FeCl$_3$	Fibres	[40]
PANI nanoadsorbent	a, APS, stabiliser	Spherical particles	[41]
PANI/tin(II) molybdophosphate	In-situ method	Spherical particles	[42]
PANI/Fe^0	a, FeCl$_3$	Fibrous structure	[43]
PANI/ZrO$_2$	Direct mixing, APS	Irregular rougher surface	[44]
PANI–ZnO	a, APS	Flaky structure	[45]
PANI/SiO$_2$	a, APS, NaCMCNa	Uniform spherical particles	[46]
Fe$_3$O$_4$/G/PANI	a, APS	Mixture of sheets and spherical particles	[47]
PANI/zeolite	a, APS	Mixture of sheets and tubular particles	[48]
PANI/MnO$_2$/TiO$_2$	a, KMnO$_2$	Aggregated spherical particles	[49]
PPy-PANI/Fe$_3$O$_4$	a, FeCl$_3$	roughly spherical particles	[3]

a = in-situ polymerisation, NaCMCNa = sodium carboxymethyl cellulose sodium.

Table 1.
Some of PANI nanocomposites and their reported structures.

4. Polyaniline and its composites for wastewater treatment

The application of PANI for wastewater treatment has been widely studied owing to its exceptional structure that comprises abundant amine and imine functional groups [50, 51]. The nitrogen atoms on these functional groups have lone pairs of electrons to facilitate chelation and adsorption of pollutants [28, 52]. However, PANI has disadvantages such as poor mechanical properties and processability as well

as low solubility. These limitations emanate from its high conjugation and strong electrostatic interaction between chains, which decreases its performance and limit its commercial application [51, 53]. Composites formation offers potential in addressing the above shortfalls. Polyaniline composites can be regarded as a material consisting of PANI matrix and one or more components such as semiconductors, metal nanoparticles, organic compounds, inorganic compounds as well as biological and natural products in order to improve polymer backbone properties or extend its functionalities [51, 54]. In order to prepare the composite materials successfully, several methods like physical mixing, sol–gel technique, *in–situ* chemical polymerisation, emulsion technology, sonochemical process and irradiation technique are employed [55]. Since then, various PANI composites have been reported for the removal of pollutants from wastewater using membrane technology [56, 57], chemical reduction [50], photocatalytic degradation [58, 59] and adsorption technology [60, 61]. Among these methods, adsorption has been identified as a prestigious technology, due to its flexibility and simplicity of design, initial cost, ease operation and insensitivity to toxic pollutants [62]. Different polyaniline-based composites for adsorption of pollutants have been widely studied. Samani et al. [60] reported PANI/PEG (polyethylene glycol) composite for the removal of hexavalent chromium ions (Cr(VI)), which had the maximum adsorption capacity (q_{max}) of 68.97 mg/g. Debnath et al. [63] reported a PANI/lignocellulose composite with q_{max} of 1672.5 mg/g for Congo red (CR) removal. PANI/chitosan was studied by Janaki et al. [64] for the removal of dyes (CR, Coomassie Brilliant Blue (CBB), and Remazol Brilliant Blue R (RBBR)). They obtained the maximum capacities to be 322.58, 357.14 and 303.03 for CR, CBB and RBBR, respectively. PANI/silica (SiO_2) gel was reported by Karthik et al. [52] with q_{max} = 63.41 mg/g for the removal of Cr(VI). However, most of these PANI composites have lower removal efficiency and adsorption capacity, owing to their irregular structure resulting from agglomeration, poor water dispersion and reduced surface area [35]. Numerous researches have been focussed on the development of nanostructured PANI composites with improved surface area and maximum adsorption capacity [35, 53, 65, 66].

5. Application of polyaniline nanocomposites as adsorbents for water treatment

In recent years, polyaniline nanocomposites have been used as adsorbents for the removal of various pollutants from wastewater [30]. More studies have been focussed on the adsorption of organic dyes and heavy metals ions due to their good interaction with PANI nanocomposites functional groups [52]. In the study of interaction between PANI nanocomposites and pollutants, various adsorption parameters such as pH, contact time, adsorbent dose, temperature, nature of the adsorbent and concentration of the pollutants are investigated [38]. From these parameters, the efficiency and adsorption capacity of nanocomposites can be determined to confirm the potential of the PANI nanocomposites as adsorbents for water purification.

5.1 Adsorption of heavy metals

The general sources of heavy metals are weathering of rocks due to their abundance in nature and mining industries as a result of mineral process of metal ores [61]. Various heavy metals known to pollute water include nickel, cadmium, lead, mercury, chromium, arsenic and copper. The water pollution by these toxic metals is a global concern owing to their acute toxicity and enduring accumulation [67].

Heavy metals are problematic since they are mutagenic, carcinogenic, are not biodegradable and can form various species [68].

5.1.1 PANI nanocomposites for adsorption of heavy metals ions

A PANI/RGO nanocomposite was reported by Li *et al*. [32] for the removal of Hg(II) ions from aqueous solution. It was shown that the PANI/RGO had high equilibrium adsorption capacity in comparison to PANI (**Figure 4a**). The obtained monolayer maximum adsorption capacity was 1000 mg/g at pH 4, 33°C and 400 mg/L for 200 mg adsorbent dose. Bhaumik *et al*. [38] reported a PANI/Fe^0 nanocomposite for the removal of arsenic (As), which had Langmuir maximum adsorption capacity of 232.5 and 227.7 mg/g for both As(III) and As(V) at pH 7, 25°C and 1 mg/L for 10 mg of PANI/Fe^0 nanocomposite. The obtained pH effects results (**Figure 4b**) showed higher removal efficiency by the nanocomposite in comparison to the neat PANI. Harijan and Chandra [33] reported a PANI/GO for the removal Cr(VI) from aqueous solution. It was demonstrated that the nano-composite had high Langmuir maximum capacity of 192 mg/g at pH 6.5, 30°C and 100 mg/L for 25 mg of PANI/GO in comparison to the neat PANI (**Figure 4c**). **Table 2** shows some of the PANI nanocomposites reported for removal of various heavy metal ions under different experimental conditions.

5.2 Adsorption of organic dyes

Organic pollutants are generally materials that comprise of aromatic rings in their structure. Numerous organic pollutants including dyes, chlorinated, aliphatic and phenolic compounds are carcinogenic and mutagenic [70]. Dyes are of major concern due to their wide application in textile, paper, pigment and plastic indus-tries. Their presence in water systems results in water decolouration, which can
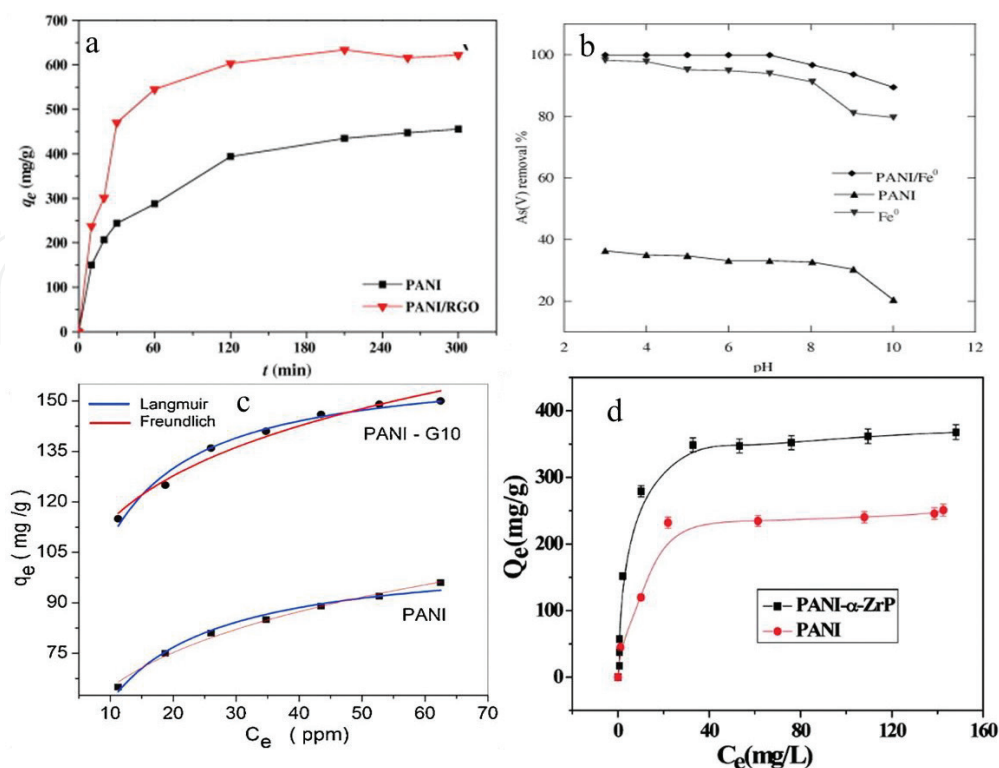

Figure 4.
Comparison of PANI and PANI nanocomposites for the removal of various pollutants (a) kinetics [32], (b) pH effect [43], (c) isotherms [33] and (d) equilibrium adsorption capacity [34].

Adsorbent	Pollutant	q_{max} (mg/g)	pH	Conc. (mg/L)	Adsorbent dose (mg)	Refs.
PANI/PAN	Cr(VI)	67.03	2	5	10	[28]
PAMpDA@Fe$_3$O$_4$	Co(II)	116.3	6	50	50	[69]
PPy-PANI/Fe$_3$O$_4$	Cr(VI)	303.0	2	100	50	[3]
Fe$_3$O$_4$/GO/PANI	Cr(VI)	153.4	6.5	100	50	[47]
PANI@Ni(OH)$_2$	Cr(VI)	625.0	4	100	10	[2]
PANI/zeolite	Cr(VI)	—	2	50	200	[48]
PANI/PVP	Mn(II)	50.30	7	100	250	[31]

Table 2.
Some of the PANI nanocomposites for heavy metals adsorption.

Adsorbent	Pollutant	q_{max} (mg/g)	pH	Conc. (mg/L)	Adsorbent dose (mg)	Refs.
PANI/MWCNTs	CR	147	2	50	7	[74]
PANI/PA 6	MO	48.8	—	10	30	[54]
ZnFe$_2$O$_4$-PANI	Rhodamine B RHB	1000	2	10	500	[29]
PANI/CMC/TiO$_2$	CR	94.28	2.6	82	140	[30]
PANI/Fe^0	CR	99.6	7	100	1000	[75]
PPy–PANI NFs	CR	222.22	4	200	1000	[35]
Starch/PANI	Reactive Black 5	811.30	5	10	60	[76]

Table 3.
Some of the PANI based nanocomposites for dye adsorption.

negatively affect aquatic life by influencing the photosynthetic process [71]. Some of PANI based nanocomposites for dye removal are given in **Table 3**.

5.2.1 PANI nanocomposites for adsorption of dyes

Wang et al. [34] reported PANI/α-ZrP for the removal of methyl orange (MO) cationic dye. It was demonstrated by **Figure 4d** that the nanocomposite (5 mg) had high removal efficiency capacity at pH 4 and 25°C for 100 mg/L MO solution. The monolayer maximum adsorption capacity was obtained to be 377 mg/g. Tanzifi et al. [46] reported PANI/SiO$_2$ nanocomposite for the removal of amido black 10B. The obtained Langmuir maximum adsorption capacity was 42.24 mg/g at pH 2, 25°C and 30 mg/L for a 100 mg adsorbent dose. Gharbani [37] reported PANI/tin(II)molyb-dophosphate for the removal of malachite green (MG). It was demonstrated that the removal efficiency was 93% for 50 mg/L of MG at pH 10 and the adsorption process followed Freundlich isotherm model. In another study, Ballav et al. [72] synthesised PANI coated ligno-cellulose composite (PLC) via in-situ polymerisation of aniline monomer for the removal of Reactive Black 5 (RB-5) from aqueous solutions. The authors reported that the equilibrium adsorption isotherm studies revealed that the Langmuir isotherm provided the best fit with monolayer adsorption capacity of 312 mg/g. The Maity's research group also reported the use of PANI-coated lignin-based adsorbent for the uptake of reactive dye eosin yellow (EY) from aqueous

solution [73]. The adsorption capability of the adsorbent was found to be more effective than the unmodified adsorbent at lower pH.

6. Conclusions

This chapter encompasses the work done on PANI nanocomposites/nano-structures for the removal of heavy metal ions and dyes from aqueous solution. Adsorption technology was widely studied due to its flexibility in design and operational simplicity. The use of PANI nanocomposites as adsorbents has been investigated for adsorption of pollutants owing to their inherent properties such as high surface area, environmental stability, easy preparation and good water dispersion. The literature showed that a variety of morphological structures can be obtained, which depend strongly on the method of synthesis, and thus have various effects on the adsorption of the pollutant. For example, PANI based nanocomposites and nanostructures are preferable prepared via in-situ polymerisation. It was demonstrated that the pH, contact time, temperature, adsorbent dosage, concentration, nature of adsorbent and the presence of competing ions have an influence on the removal efficiency of nanocomposites. Hence, optimisation of adsorption parameters has been studied for the removal of heavy metals such Cr(VI), Hg(II), As(V), Co(II) and dyes such as CR, MB, MO, MG and RB5 from wastewater using various PANI nanocomposites and nanostructures. Overall, these nanocomposites display improved removal efficiency towards heavy metals and dyes adsorption. Hence, data in this chapter provides insight into PANI based materials for potential use as economically valuable adsorbents for the removal of dyes and heavy metals ions from wastewater.

Acknowledgements

Conflict of interest

We declare that there is no conflict of interest.

Author details

Thabiso C. Maponya[1,2], Mpitloane J. Hato[1,3]*, Thabang R. Somo[1],
Kabelo E. Ramohlola[1], Mogwasha D. Makhafola[1], Gobeng R. Monama[1],
Arjun Maity[2], Kwena D. Modibane[1]* and Lebogang M. Katata-Seru[4]

1 Department of Chemistry, School of Physical and Mineral Sciences, University of
Limpopo (Turfloop), Sovenga, Polokwane, South Africa

2 DST/CSIR Innovation Centre, National Centre for Nanostructured Materials,
CSIR Materials Science and Manufacturing, Pretoria, South Africa

3 Department of Environmental Sciences, College of Agriculture and
Environmental Sciences, University of South Africa (UNISA), Florida Science
Campus, Johannesburg, South Africa

4 Department of Chemistry, School of Physical and Chemical Sciences, North West
University, Mmabatho, South Africa

*Address all correspondence to: mpitloane.hato@ul.ac.za
and kwena.modibane@ul.ac.za

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