

Adsorption of Toxic Metals on Modified Polyacrylonitrile Nanofibres: A Review

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Abstract Removal of toxic metals from aqueous solutions is of high priority in environmental chemistry. Most of the available techniques for this task are considered expensive; however, the adsorption process has been considered the easiest and the cheapest way of removing toxic metals from aqueous solution. The performance of adsorption setup largely depends on the characteristic of adsorbents. One of these characteristic is availability of large surface area. The more the available sites for chelation, the more the amount of metals removed. Therefore, the production of materials of nanoscale is expedient for adsorption purposes. Electrospinning process is one of the technologies that have been employed to produce polyacrylonitrile nanofibres (PAN-nfs). Moreover, PAN-nfs surfaces have also been chemically modified so as to introduce chelating groups such as amine, carboxyl, imines, etc. Here we review PAN-nfs as metal ion adsorbent. With characteristics such as high surface area as well as good mechanical strength, modified PAN-nfs are considered good adsorbents and have been used to remove toxic metals such as cadmium, lead, chromium, mercury, uranium, silver and copper in different ion states from

their aqueous solutions. The ease of immobilization of metal-specific ligands on PAN-nfs has been of great interest in selective extraction of metal ions from their aqueous solutions. Also, toxic metals adsorbed on modified PAN-nfs can be recovered through desorption process using acids or bases of various concentrations.

Keywords Adsorption · Toxic metals · Polyacrylonitrile · Electrospinning · Nanofibres · Chelating groups

1 Introduction

Nowadays, the increase in industrial effluents is causing serious environmental contamination and the treatment of these effluents and the already contaminated environments is of great concern globally. Among the constituent of the effluents are toxic as well as precious metals (Winde and Sandham 2004; Winde 2006; Tutu et al. 2008). Several techniques have been used to remove toxic metals from contaminated water. These techniques include ion-exchange, chemical precipitation, coagulation-flocculation, flotation, membrane filtration, electrochemical treatment, reverse osmosis and adsorption (Kurniawan et al. 2006; Fu and Wang 2011). Among these techniques, adsorption is arguably the simplest and most effective technique and its efficacy largely depends on the fabrication of high capacity adsorbents (Fu and Wang 2011). Adsorption has been used to remove toxic metal ions from various aqueous solutions even at low concentrations (Neghlani et al. 2011). In

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fact, adsorption can deal with a wide range of target pollutants (inorganics and organics in wastewater treatment) with high capacity and fast kinetics (Fu and Wang 2011). The performance of these adsorbents largely depends on their physical and chemical properties. It is noteworthy that adsorption is a surface phenomenon and therefore the efficiency of adsorbents largely depends on their ability to adsorb metal ions from the solutions onto their surfaces in order to remove the metal ions from the solution. However, the purpose of adsorption is not to permanently keep the metal ions (chemisorption) on the adsorbents, but rather, adsorbents should be able to release the metals afterwards (physisorption). This is important for the purpose of recovery of metals and regeneration of adsorbents (Kampalanonwat and Supaphol 2014; Hong et al. 2015).

Adsorbents in the nano-size range are considered excellent simply because of their large surface area which allows fast and high adsorption capacities (Deng and Bai 2003; Saeed et al. 2008). Because of characteristics such as large surface area, chemical resistance, thermal stability, low flammability as well as good mechanical properties, modified PAN nanofibres (PAN-nfs) have been recognized as highly efficient materials for the removal of toxic metal ions from solutions with high adsorption capacity and fast adsorption equilibrium (Deng et al. 2003a; Saeed et al. 2008; Neghlani et al. 2011).

There is a lot of interest in modifying PAN-nfs for the adsorption of toxic metals. This is because for effective adsorption, adsorbents are preferred to be water loving (hydrophilic) and must possess active chelating groups. It is only the surface modification of PAN-nfs that can bring about these characteristics. By virtue of the presence of nitrile groups on PAN-nfs surfaces, several surface chemical modifications have been done to introduce chelating functional groups. These chelating functional groups include amidoxime (Pekel and Guven 2003; Saeed et al. 2008; Horzum et al. 2012), imidazole (Pekel et al. 2000), metal oxides (Zou et al. 2009; Comarmond et al. 2011; Sadeghi et al. 2012), carboxyl or phosphoryl derivatives (Yakshin et al. 2010) and pendant amine groups (Deng et al. 2003a; Kampalanonwat and Supaphol 2010, 2014; Neghlani et al. 2011; Hong et al. 2015). These functional groups came about as results of chemical reactions such as amination, amidoximation and hydrolysis. Amination involves the grafting of amine-containing ligands on the surfaces of PAN-nfs (Deng et al. 2003a; Neghlani

et al. 2011). The grafting reactions were reported to take place on the carbons of the nitrile groups. In particular, the amine group introduced on PAN-nfs has been found to be one of the most effective chelating groups for adsorption of toxic metal ions from aqueous solutions (Ng et al. 2002; Deng et al. 2003a; Kampalanonwat and Supaphol 2014; Hong et al. 2015). The amidoximation reaction allows the introduction of amine and oxime groups to the surface of PAN-nfs (Saeed et al. 2008; Feng et al. 2011; Horzum et al. 2012). This is achieved through the reaction between the nitrile groups of PAN-nfs and hydroxylamine. PAN-nfs have also been hydrolyzed using NaOH/KOH (Gupta et al. 2004; Deng et al. 2003b; Kampalanonwat and Supaphol 2011). Selectivity of the modified PAN-nfs towards a specific metal ion depends on the pH of the aqueous solution and the functional group on the PAN-nfs. Moreover, selectivity can be achieved by immobilizing ligands that have been previously used in liquid-liquid extraction and are proven to be selective towards a specific metal ion on PAN-nfs (Ndayambaje et al. 2016). The resultant nanofibres were found to possess carboxyl and imine groups. To the best of the authors' knowledge, no literature review has been published on the adsorption of toxic metals with various modified PAN-nfs. This article presents a review of the various metals that have been adsorbed by modified PAN-nfs with their adsorption conditions.

2 Surface Modified PAN-nfs as Adsorbents

Chelation and ion-exchange have been considered as the critical adsorption mechanisms for toxic metal ions on various adsorbents (Chen et al. 2002; Jin and Bai 2002). It has been reported that the presence of carboxyl, sulfonic and phosphonic groups on the surface of adsorbents favour metal ion adsorption via the ion-exchange mechanism, while the presence of nitrogen containing groups such as amino, hydrazine, thioamide and imidazoline allows metal ion adsorption through the chelation mechanism (Coskun et al. 2000; Lacour et al. 2001; Chen et al. 2002; Jin and Bai 2002; Ndayambaje et al. 2016). In adsorption process, metal ions in the aqueous solutions are transported via diffusion or convection to the surfaces of the adsorbents and the metal ions get attached to the functional group(s) on the surface of the adsorbents.

Toxic metals ions such as lead, cadmium, copper, mercury, uranium, etc. have been adsorbed from their

aqueous solutions with various modified PAN-nfs (Deng et al. 2003a; Saeed et al. 2008; Neghlani et al. 2011; Horzum et al. 2012; Bode-Aluko et al. 2016; Pereao et al. 2016). The adsorption studies were carried out by investigating parameters such as pH, initial concentration of metal ions, contact time, adsorbent dosage and temperature. So also, adsorption models such as isotherms, kinetics and thermodynamics parameters were used to determine the efficiency of the adsorption process. Table 1 presents the comprehensive details of previously adsorbed metal ions with the adsorption parameters ranging from the nature of adsorbents, the pH of adsorptions, the capacity of the adsorbents, etc. Furthermore, the interactions between the chelating groups and the metal ions were studied using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) and X-ray photoelectron spectroscopy (XPS) techniques (Deng et al. 2003a; Neghlani et al. 2011; Hong et al. 2015).

2.1 Batch and Column Adsorption Techniques

Functionalized PAN-nfs have been used in both batch and column adsorption techniques and are found to be effective (Neghlani et al. 2011; Horzum et al. 2012). In the column technique (flow continuous), the modified PAN-nfs were placed in a vertical column to form a bed and the aqueous solution containing the metal ions was run through the column (Horzum et al. 2012). However, in the batch technique, modified PAN-nfs were placed in a vessel containing the metal ions solution and shaken together over a period of time (Deng et al. 2003a; Saeed et al. 2008; Neghlani et al. 2011). After the adsorption process using either technique, the modified PAN-nfs can be regenerated and be reused in another cycle. The regeneration will be discussed later in the review.

2.2 Effect of pH Values

The most important factor in adsorption studies is the pH of the aqueous solution. The pH has effects on both the adsorbents and the metal ions in the solution. The chelating functional groups of the adsorbents can undergo dissociation at certain pH and also the surface charges can be affected. Therefore, stability tests are carried out on modified PAN-nfs in different pHs especially in acidic medium in order to make sure that the surface modified PAN-nfs retains its functionality throughout the adsorption process. It has been generally

explained that the pH of the solution affects the adsorptive process because of the protonation and deprotonation of the acidic and basic groups of the chelating ligands (Deng et al. 2003a; Neghlani et al. 2011; Horzum et al. 2012). At lower pH, the functional groups (active sites) of the adsorbent are less available for metal ions due to protonation of the active sites at higher H^+ concentration. As the pH increases, the degree of protonation of the surface functional groups gradually reduces and approaches zero resulting in a gradual increase in the adsorption. Furthermore, pH affects the existent state of metal ions in solution to a certain extent. Metal ions are readily available for adsorption as pH increases. However, to prevent the metal ions from precipitation, a pH of greater than 7.0 is often not studied (Soltanzadeh et al. 2013). The pH of the adsorption setup is often adjusted with 0.1 M HCl or 0.1 M NaOH especially when using modified PAN-nfs as adsorbents (Ndayambaje et al. 2016).

Generally, higher adsorptions of metal ions are observed at higher solution pH values in the acidic region; meanwhile, chemical precipitation at higher pH must be avoided, so that removal could be related to the adsorption process and not precipitation (Fu and Wang 2011). Deng et al. (2003a) modified PAN-nfs with diethylenetriamine (PAN-DETA) for lead and copper ions. At pH below 2.3, almost no adsorption of lead and copper ions took place. A similar situation arose when Neghlani et al. (2011) used the same adsorbent for copper ions. This may be due to the protonation of the amine groups of PAN-DETA. As the pH increases from 2.3 to 3, the amount of copper ions adsorbed on the PAN-DETA increased and then appeared to approach a plateau, no further noticeable increase was observed for pH from 3 to 6 (Deng et al. 2003a). It was explained that, at higher pH, more amine groups are available to capture the metal ions (i.e., via the interaction of the metal ions with the lone-pair electrons of nitrogen). It may also be possible that when pH was below 2.3, the strong electrical repulsion prevented the metal ions from contacting the surfaces of the PAN-DETA, resulting in almost no adsorption of lead or copper ions on the PAN-DETA. With the increase of solution pH values, the electrical repulsion force became weaker and the metal ions may be transported to the surface of the PAN-DETA and become attached on the surface (Deng et al. 2003a; Neghlani et al. 2011). Kampalanonwat and Supaphol (2010) also used PAN-DETA for Cu(II), Ag(I), Fe(II) and Pb(II) adsorption. Increasing the initial

Table 1 Adsorption studies of toxic metals on various modified PAN-nfs

Adsorbents	Techniques	Metals	Optimum pH	Quantity adsorbed	Authors
PAN-TETA	Batch	Cu(II), Cd(II)	6	Cu, 109; Cd, 99 mg/g	Soltanzadeh et al. (2013)
PAN-TETA	Batch	Cr(VI)	5	133 mg/g	Wang et al. (2011)
PAN-DETA	Batch	Pb(II), Cu(II)	4.5	Pb, 76; Cu, 31 mg/g	Deng et al. (2003a)
PAN-TEPA	Batch	Cr(VI)	1	33.2 mg/g	Chen et al. (2014)
PAN/PMMA TEPA	Batch	Cr(VI)	1	49.8 mg/g	Chen et al. (2014)
PAN-DETA	Batch	Cu(II), Ag(I), Fe(II), Pb(II)		Cu, 150; Ag, 155; Fe, 116; Pb, 60 mg/g	Kampalanonwat and Supaphol (2010)
PAN-DEDA	Batch	CrO ₄ ²⁻ , PO ₄ ³⁻	CrO ₄ ²⁻ ; 1.02; PO ₄ ³⁻ ; 2.89	CrO ₄ ²⁻ , 5.7; PO ₄ ³⁻ , 3.8 mmol/g	Ko et al. (2004)
PAN-DEDA	Batch	Cu(II), Ni(II), Fe(II), Ag(I)		Cu(II), 4.49; Ni(II), 1.91; Fe (II), 3.76; Ag(I), 5.1	Ko et al. (2004)
PAN-DEDA	Batch	Cu	6	11.6 mg/g	Neghlani et al. (2011)
PAN + NHOH	Batch	Cu(II), Fe(III)		Cu, 215; Fe, 221 mg/g	Huang et al. (2013)
PAN + NHOH	Batch	Cu(II), Pb(II)		Cu(II), 52.7; Pb(II), 263.45 mg/g	Saeed et al. (2008)
PAN + NHOH	Batch	Cu(II), Cd(II)		Cu(II), 3.44; Cd(II), 4.55 mmol/g	Feng et al. (2011)
PAN + NHOH	Column	U(VI)	4	85%	Horzum et al. (2012)
PAN-OH	Batch	Cu(II)	4.5	27.95 mg/g	Deng et al. (2003b)
PAN-OH	Batch	Cu(II)	5	31.3 mg/g	Kampalanonwat and Supaphol (2011)
PAN-H	Batch	Cu(II), Pb(II)		Cu(II), 114; Pb(II), 217 mg/g	Saeed et al. (2011)
PAN-8Q	Column	Cu(II)	6	246 mol/g	Wen and Shan (2002)
PAN-PPy	Batch	Cr(VI)	2	65.5 mg/g	Wang et al. (2014)
PAN-DETA	Batch	Pb(II)	5.5	1520 mg/g	Hong et al. (2015)
PAN-PIM	Batch	Ni(II)	5	0.7 mol/kg	Ndayambaje et al. (2016)

PAN-TETA triethylenetetramine, *PAN-DETA* diethylenetriamine, *PAN-TEPA* tetraethylenepentamine, *PAN/PMMA-TEPA* poly(methyl methacrylate), *PAN-DEDA* diethylenediamine, *PAN+NHOH* amidoximated PAN, *PAN-OH* hydrolyzed PAN, *PAN-H* hydrazine, *PAN-8Q* 8-hydroxyquinoline, *PAN-PPy* polypyrrole PAN, *PAN-PIM* PAN-2-(2-pyridyl)imidazole

pH of the testing solutions resulted in the amounts of the adsorbed metal ions reaching plateau values, and in most cases (except for the adsorption of Ag(I) ions), the amounts of the adsorbed metal ions decreased as the initial pH approached neutrality. This could be due to the competitive adsorption of the OH ions via the formation of the hydrogen bond, resulting in the reduction of the adsorptive sites on the surface of the PAN-DETA nanofibres. Moreover, at higher pH levels, the concentration of OH ions is high enough to interact with the metal ions, reducing the availability of the metal ions in their free, hydrated form to interact with the amine groups of the DETA ligands. Soltanzadeh et al. (2013) modified PAN-nfs with triethylenetetramine (PAN-TETA) and used it as adsorbent for copper and cadmium ions. Lower uptakes of both metals were observed at

lower pH. This may be attributed to the partial protonation of the active groups and the competition of H⁺ with metal ions for adsorption sites on the PAN-TETA. Adsorption efficiency increased with increased pH and maximum sorption was achieved at pH 6. At this pH, the adsorbent is selective for Cu (Soltanzadeh et al. 2013). Deng et al. (2003b) hydrolyzed PAN-nfs with NaOH for copper ion adsorption. At a pH less than 3, the amount of adsorption was very low (less than 2.8 mg/g), but the amount of adsorption increased sharply at a pH between 3.0 and 4.0 and reached up to 12.4 mg/g. However, no further increase of adsorption was observed for a pH increase between 4.0 and 6.0. Horzum et al. (2012) introduced amidoxime groups on the surface of PAN-nfs for uranium ions adsorption. The percent UO₂²⁺ uptake increased as pH levels increased from 3.0 to

4.0. The amidoximated PAN nanofibres seemed to demonstrate maximum sorption at pH 4.0. At this pH, the UO_2^{2+} ion is the main species (approximately 85%) among other chemical forms. At lower pH, uranium is still present in the form of free UO_2^{2+} ions; however, competitive sorption with protons occurs and ion-exchange interactions are favoured (Sylwester et al. 2000). Protonation can occur on the amino group of amidoxime (pKa 5.95) leading to a decrease in the chelating ability. Kampalanonwat and Supaphol (2011) also modified PAN-nfs in sodium hydroxide ethanolic/aqueous solution for adsorption of copper ions. A low adsorption was observed at low pH which was due to the competitive adsorption between the prevalently available H^+ and the Cu ions. The electrostatic repulsion between the protonated imine groups of the modified PAN-nfs and copper ions could be another reason for the very low adsorption values. The decrease in the amount of H^+ , as the initial pH increased, resulted in less competitive adsorption on the available adsorptive sites as well as an increase in the number of the available adsorptive sites as the protonation of the imine groups on the hydrolyzed PAN-nfs decreases. Away from this trend, Chen et al. (2014) used tetraethylenepentamine PAN-nfs (PAN-TETA) for chromium adsorption. Good adsorption was observed at low pH. They proposed that H^+ was preferably adsorbed to the surface of PAN-TETA causing the protonation of amine groups, which in turn favoured the sorption of anionic Cr(VI) species (such as HCrO_4^- and CrO_4^{2-}) (Wang et al. 2011). At high pH values, the H^+ concentration significantly reduced and consequently decreased the adsorption of chromium. Similar pH patterns were reported for Cr(VI) sorption by aminated PAN-nfs (Deng and Bai 2004), anion-exchange resins (Shi et al. 2009) and amine-modified celluloses (Anirudhan et al. 2009).

2.3 Point of Zero Charge

The point of zero charge (pzc) of a material is where the electrical charge density on a surface of the material is zero. In adsorption, the point of zero charge determines how easily a substrate is able to adsorb metal ions. Pzc is equivalent to the pH value only when H^+/OH^- are the potential determining ions. Deng et al. (2003b), in their adsorption experiments of copper ions using hydrolyzed PAN-nfs (HPAN-nfs), observed that the point of zero potential of the nanofibres is at pH about 5.3. When the solution pH values are below 5.3, the pzc of the HPAN-

nfs are positive and therefore the interaction between copper ions and the surface of the HPAN-nfs is electrostatically repulsive. Decreasing the solution pH increases the repulsive force between copper ions and the surface of the HPAN-nfs and thus inhibits the transport of copper ions from the bulk solution to the surface of the HPAN-nfs for adsorption to take place. Deng et al. (2003a) prepared aminated PAN-nfs with diethylenetriamine for adsorbing lead and copper ions from aqueous solutions. It was found that the pzc of the aminated PAN-nfs was at about pH 8.1, in contrast with that of the pristine PAN-nfs at pH 3.6, and the aminated PAN-nfs had significantly higher adsorption capacities for both lead and copper ions than the pristine PAN-nfs. The literature on the pzc studies of modified PAN-nfs are few and are rarely studied.

2.4 Initial Concentration

The initial concentration of a model toxic metal ion solution for adsorption is usually prepared in parts per million (mg/L). For effective application of adsorbents towards environmental remediation, the initial metal concentration is usually prepared relative to the World Health Organization (WHO) standards. In adsorption studies of modified PAN-nfs, it is generally noticed that the amount of metal ions adsorbed increase with an increase in the initial concentration of the metals ions. At a certain point, the concentration might attain a saturation plateau where there will be no space on the adsorbent to adsorb (Deng et al. 2003a; Horzum et al. 2012; Soltanzadeh et al. 2013). Soltanzadeh et al. (2013) and Deng et al. (2003a) showed that the amount of copper adsorbed on PAN-TETA increased with an increase in the initial concentration. This was also reported by Deng et al. (2003b) when they used hydrolyzed PAN for removal of Cu. Horzum et al. (2012) showed that the amount of adsorbed uranyl ions on amidoximated PAN-nfs increased with the increase in the initial concentration of uranyl ions. Feng et al. (2011) also observed the same trend for Cu(II) and Cd(II) on amidoximated PAN-nfs (AMPAN-nfs). The initial increase in metal ion adsorption might be attributed to many available amidoxime groups in AMPAN-nfs. However, as more sites in the amidoxime groups were filled, it became difficult for more metals ions to find vacant sites. At the same time, the amount of metal ions adsorbed reached saturation sooner with an increase in the concentration of metal ions (Feng et al. 2011; Horzum et al. 2012).

2.5 Contact Time

It is a usual trend in adsorption studies that as the contact time increases, there is also an increase in amount of metal ions adsorbed. This is mainly due to a sufficiently large surface area and the availability of active sites of the adsorbent at the beginning of the adsorption process. The contact time could also be related to protonation time; as the time increases, the protonation time also increases and the H^+ takes up the adsorption sites blocking other metal ions from being adsorbed (Wang et al. 2014). Neghlani et al. (2011) observed that the amount of Cu(II) adsorbed onto the PAN-DETA increased rapidly in the first 20 min and then levelled off. Saeed et al. (2011) modified PAN-nfs with hydrazine for adsorption of Cu(II) and Pb(II) ions in aqueous solution. The amount of adsorption of both metal ions increased as the adsorption time increased. Kampalanonwat and Supaphol (2010) also observed that an increase in the contact time also resulted in a monotonous increase in the amounts of the metal ions adsorbed on PAN-DETA, which finally reached equilibria at about 5 h for Ag(I), Fe(II), Pb(II) and 10 h for Cu(II). The removal rate of Cr(VI) by PAN-TETA versus sorption time as plotted by Wang et al. (2011) showed that the sorption equilibrium was reached very fast and took only about 10 min. Kampalanonwat and Supaphol (2011) showed that for hydrolyzed PAN-nfs, the amounts of the Cu(II) ions adsorbed increased with an initial increase in contact time at the optimal pH of 5.0. The plateau values were reached after about 5 h of immersion of HPAN-nfs.

2.6 Amount of Adsorbents

The amount of modified PAN-nfs is rarely studied in adsorption. Meanwhile an increase in the amount of adsorbent would translate to an increase in the number of adsorption sites and thereby increase the adsorption of metal ions. Contrary to this, Soltanzadeh et al. (2013) reported that with the increase of adsorbent dosage (PAN-TETA) from 0.1 to 0.3 g, the copper ions sorption capacity decreased from 49.3 to 16.39 mg/g, while the cadmium ions sorption capacity decreased from 39.73 to 13.2 mg/g. It was attributed to the aggregation of adsorbent particles at high dosage, which reduced the total surface area of the adsorbent and resulted in an increase in the diffusion path length. In the case where the initial concentration of metal ion is kept constant, an

increase in the amount of adsorbent would lead to a large number of sites available for a fixed concentration of metal ions (Soltanzadeh et al. 2013), meaning that saturation of the sites would not occur and the excess capacity of the adsorbent would be wasted.

3 Desorption and Regeneration of Adsorbents

Desorption of toxic metals from various modified PAN-nfs is carried out in order to recover the adsorbed metals and also to regenerate the adsorbents. Most desorption processes are carried out with acids or bases of different molar concentrations. This process must be carefully studied and optimized so as to avoid damage to the adsorbents by the regenerating agents. Kampalanonwat and Supaphol (2010) regenerated PAN-DETA with HCl of concentrations ranging from 2.0 to 10.0 M after batch adsorptions of Cu(II), Ag(I), Fe(II) and Pb(II). Desorption of metal ions was carried out in 20 mL of each concentration of HCl. The results obtained showed that desorption efficiency of over 90% was achieved for all the metals with 10 M HCl solution. Saeed et al. (2008) also carried out desorption test on amidoximated PAN-nfs after adsorption of Cu(II) and Pb(II) using 1 M HNO_3 . Desorption percentages were 40 and 58, respectively, within 2 min, and after 1 h, the amount of recovered metals was over 90%. As reported by Feng et al. (2011), Cu(II) and Cd(II) were desorbed from amidoximated PAN-nfs using 1 M HNO_3 . The results showed 87% (Cu) and 92% (Cd) after 60 min.

Desorption tests on uranyl ion loaded amidoximated PAN-nfs as carried out by Horzum et al. (2012) showed that chelating agents can be a good regenerating agents. $NaHCO_3$, EDTA and ammonium citrate were used as chelating agents for the release of uranyl ions and the regeneration of the adsorbent. The desorption percentages of U(VI) were 80% for 0.5 M $NaHCO_3$, 45% for 0.5 M ammonium citrate and 34% for 0.1 M EDTA. Therefore, $NaHCO_3$ was adjudged as the desorbing eluent due to its relatively higher desorption yield. It was further explained that uranium forms negatively charged or neutral carbonate complexes and the adsorbed uranyl ions could be eluted from the sorbent using $NaHCO_3$ through the addition of carbonate ions as ligands to complex uranyl ions. After five cycles, the efficiency of sorption decreased from 86.0 to 59.5% while the recovery of U(VI) decreased from 80.0 to 55.0%.

Deng et al. (2003b) hydrolyzed PAN-nfs with NaOH for removal of copper ions and subsequently desorbed the metal ions using deionized water and 1 M HCl. Of the copper ions, 3.6% was desorbed in deionized water in the first 10 min, but desorption did not increase further after 10 min. However in 1.0 M HCl, up to 89% of the adsorbed copper ions was desorbed within 2 min, and the percentage of desorption reached 98% after 30 min. Kampalananwat and Supaphol (2011) also hydrolyzed PAN-nfs with NaOH in ethanolic/aqueous for removal of Cu ions. Desorption was likewise carried out in deionized water and 1.0 M HCl. The results were in agreement with the previous report by Deng et al. (2003b). Saeed et al. 2011 adsorbed Cu and Pb using hydrazine-PAN-nfs adsorbents. Desorption of the metal ions from metal-loaded hydrazine-PAN-nfs was carried out using 1.0 M HNO₃. Desorption percentage of Cu(II) and Pb(II) were 52 and 73%, respectively, in 15 min. Column studies demonstrated that exhausted PAN-TETA could be completely regenerated by 0.1 M NaOH for repeated sorption of chromium for as many as 15 sorption regeneration cycles (Wang et al. 2011).

4 Determination of active Sites on Modified PAN-nfs

ATR-FT-IR and XPS analysis have been instrumental in determining the active sites of various modified PAN-nfs responsible for chelation of toxic metals (Deng et al. 2003a, b; Horzum et al. 2012; Ndayambaje et al. 2016). This helps to know the functional groups that are involved in the adsorption. ATR-FT-IR technique is used to characterize metal-ion loaded modified PAN-nfs. One can infer the point of chelation from the differences in the spectra of modified PAN-nfs and the metal-ion loaded PAN-nfs. XPS has also been used to identify the interaction of a metal ion with the surface of the PAN-nfs after adsorption (Deng et al. 2003a; Kampalananwat and Supaphol 2011). The creation of a chemical bond between a metal ion and an atom on the surface of the adsorbent changes the distribution of the electrons around the corresponding atoms, meaning that the electron-donating ligands can lower the binding energy (BE) of the core-level electrons while electron-withdrawing ligands can raise their BE (Tombacz et al. 2000; Zhang and Bai 2002, 2003).

Horzum et al. (2012) used ATR-FT-IR method to characterize the amidoximated PAN nanofibres before and after the adsorption of uranyl ions. The reaction of

hydroxylamine with nitrile groups leads to the formation of C=N groups characterized by the band at 1665 cm⁻¹ and a broad band at 3000–3700 cm⁻¹ can be attributed to H-bonding of NH₂ and O-H in the amidoxime structure. Upon the sorption of UO₂²⁺, a shift was observed in the stretching band of C-N from 1218 to 1248 cm⁻¹ to confirm an interaction between the metal ion and lone-pair electron on nitrogen atom (Horzum et al. 2012). Deng et al. (2003a) used both ATR-FT-IR techniques to analyse PAN-DETA after the adsorption of lead and copper ions from the solutions. The overlapping broad band of the NH and OH stretching vibrations on the PAN-DETA in the region of about 3100 to 3700 cm⁻¹ with a peak at 3438 cm⁻¹ shifted to 3429 and 3431 cm⁻¹ for copper and lead-loaded PAN-DETA, respectively. The decrease in peak intensities may be attributed to the attachment of the metal ions on the NH or OH groups, which affected the stretching vibration frequency of the active functional groups (Deng et al. 2003a). Similarly, the peak at 1596 cm⁻¹ for the primary amine groups on the PAN-DETA was shifted to 1588 and 1589 cm⁻¹, respectively, after the adsorption of lead or copper ions, indicating the existence of interactions between the lead and copper ions with the nitrogen atom in the NH₂ groups (Hong et al. 2015).

The XPS spectra of copper ion loaded hydrolyzed PAN-nfs as observed by Kampalananwat and Supaphol (2011) indicated specific interactions between the adsorbed Cu(II) ions and the nitrogen and/or the oxygen atoms associated with the imine groups on the surface of the hydrolyzed PAN-nfs. The N 1s spectrum of the hydrolyzed PAN-nfs showed that binding energies of imine and nitrile groups were found to be in the same region between 398.4 and 399.8 eV (Pels et al. 1995). The peak centred at 399.4 eV was assigned to the N 1s core-level spectrum of N-atoms associated with the imine conjugated sequences (Deng et al. 2003b). Additionally, the peaks centering at 400.1 and 401.3 eV could be assigned to the C-N bonding and the protonated imines (Mosser et al. 1992; Dambies et al. 2001), respectively. After the adsorption study, two deconvoluted peaks, centering at 398.4 and 399.9 eV, were observed. The presence of these peaks suggested that the adsorbed Cu(II) ions altered the electronic properties of the bound N-atoms associated with the imine conjugated sequences, causing the electrons to locate closer to the ions and, hence, increasing the N 1s binding energy. The Cu 2p_{3/2} core-level spectrum of the hydrolyzed PAN-nfs after the copper adsorption study

showed two deconvoluted peaks centering at 931.9 and 933.5 eV could be assigned to Cu(I)/Cu(0) and Cu(II), respectively (Dambies et al. 2001; Deng et al. 2003b; Martinez et al. 2011). The result suggested that, after the adsorption, some of the Cu(II) ions formed tight bonding with the N-atoms of the imine groups, causing their electron cloud densities to increase, hence the observed decrease in the binding energy (Deng et al. 2003b). The O 1s spectrum of the hydrolyzed PAN-nfs, after the adsorption, could be deconvoluted into two peaks, centering at 530.5 and 532.3 eV. While the first peak could be assigned to the OH groups that were formed onto the surface of the hydrolyzed PAN-nfs after the hydrolysis (Deng et al. 2003b), the presence of the latter peak suggested that some of the Cu(II) ions interacted with the O-atoms of these OH groups, drawing electrons closer to them and, hence, increasing the O 1s binding energy (Kampalananwat and Supaphol 2011). Similarly, Deng et al. (2003a) used XPS analyses to confirm the interaction between PAN-DETA and lead ions as well as copper ions. The N 1s core-level XPS spectra of the PAN-nfs, the PAN-DETA and the PAN-DETA adsorbed with lead or copper ions were examined. The N 1s core-level XPS spectra of the PAN-nfs could be fitted by only one peak at 398.6 eV for the nitrogen in the C≡N group. After the chemical reaction with diethylenetriamine, the N 1s core-level XPS spectra of the PAN-DETA can be assigned to peaks at the BEs of 398.6 and 399.9 eV for the nitrogen in the C≡N and NH₂ or NH groups, respectively, which indicated the presence of the amine groups on the surface of the PAN-nfs. After the adsorption of copper ions, a new peak at the BE of 401.0 eV appeared and the peak at the BE of 399.9 eV was reduced. Similarly, a new peak at BE of 400.9 eV was observed for the PAN-DETA loaded with lead ions. The XPS results hence confirmed that lead and copper ions were adsorbed to the nitrogen of amine groups on the surface of the PAN-DETA. The lone pair of electrons in the nitrogen atoms of the amine group can be donated to form a shared bond between a lead or copper ion and the nitrogen atoms. As a result, the electron cloud density of the nitrogen can be reduced

and a peak at a higher BE (i.e., at 401 or 400.9 eV) can be observed. The O 1s XPS spectra of the PAN-nfs were assigned to the two peaks at 531.8 and 533.3 eV, attributed to the oxygen in the C=O and C-O bonds of the O=C-O group in the PAN-nfs, respectively. The O 1s XPS spectra of the PAN-DETA however were assigned to the two peaks at BEs of 531.8 and 532.8 eV for the oxygen in the C=O and OH groups, respectively. After the adsorption of Cu ions on the PAN-DETA, the two initial peaks at BEs remained. This suggests that the oxygen in the two species was not involved in forming a complex with the copper ions during the adsorption. For lead ions, a new peak at BE of 533.9 eV appeared after the adsorption, and the peak at BE of 532.8 eV was reduced due to the adsorption. The results indicate that the hydroxyl groups on the surface of the PAN-DETA may be involved in the adsorption of the lead ions. The overall results revealed that lead and copper adsorption on PAN-DETA can be mainly attributed to the formation of metal complexes with the nitrogen atoms in the amine groups on the surfaces of the PAN-DETA, although the hydroxyl groups on the PAN-DETA may also be involved in binding lead ions from the solutions (Deng et al. 2003a).

5 Physical Characterization of Metal Ion Loaded Modified PAN-nfs

Researchers have also used scanning electron microscopy (SEM) and atomic force microscopy (AFM) images to support adsorption of toxic metals on modified PAN-nfs (Deng et al. 2003a; Horzum et al. 2012; Chen et al. 2014). The images from AFM as reported by Deng et al. (2003a) indicated that the PAN-DETA had a rougher surface after the adsorption of lead and copper. Neghlani et al. (2011) also reported that the AFM results of PAN-DETA and the copper ions loaded PAN-DETA. The results showed an increase in surface roughness of PAN-DETA upon adsorption of the metal ion compare to ordinary PAN-DETA. Deng et al. 2003b used hydrolyzed PAN-nfs (HPAN-nfs) for copper ions and the

Table 2 Weight percentages and atomic percentages (in brackets) of C, N, O and U in amidoximated PAN-nfs after adsorption of uranyl ions

Elements	C	N	O	U
Sampling area 1	58.69 (67.83)	26.19 (25.95)	6.60 (5.72)	8.52 (0.50)
Sampling area 2	59.62 (68.14)	26.21 (25.69)	6.70 (5.75)	7.48 (0.43)
Sampling area 3	55.62 (70.27)	20.39 (22.09)	6.87 (6.55)	17.06 (1.09)

AFM results showed that some aggregates formed on the surface of the HPAN-nfs after copper ion when compared with ordinary HPAN-nfs.

Horzum et al. (2012) determined the elemental composition of amidoximated PAN fibre after uranyl ion sorption with SEM-EDS analysis. Table 2 showed the C, N and O signals originated from the polyacrylonitrile and the presence of an uranium signal indicated that uranium was fixed on the surface of the amidoximated PAN-nfs.

Also, Horzum et al. (2012) observed the SEM images of PAN-nfs and AMPAN-nfs. The results showed no serious deterioration of the surface texture or roughness was observed after the sorption process of uranyl ion, and the morphology and the integrity of the fibres were preserved. Chen et al. (2014) reported the EDX spectra and map imaging of aminated porous PAN-nfs (APPAN) after absorption of Cr(VI) ions. The results showed that Cr(VI) was adsorbed on the fibre mat. The distribution of Cr(VI) ions on APPAN fibre mat found not to be homogeneous, possibly due to the existence of pores (Chen et al. 2014).

6 Conclusion

Various modified PAN-nfs have been used extensively for adsorption of toxic metals. This is because of the large surface area as well as the various forms of modification of the surface of PAN-nfs which introduce various functional/active sites on the nanofibres. The introduction of a preferred chelating group can be a good avenue in selecting the metals to be removed from solution even though pH of the solution may play a significant role on the oxidation state of the metals and the adsorbents. This brings to notice that for selectivity to be achieved, the adsorbents cannot be treated in isolation; such parameter as well should be taking into considerations. Selective ligands previously use in liquid-liquid adsorption for metals can be immobilized on PAN-nfs. This will give the resultant adsorbent several advantages such high as selectivity, mechanical advantage, large surface area as well as reusability. Having reported various ways of desorbing metals from modified PAN-nfs, reusability of the adsorbents is not adequately studied up till date. One would have expected that authors should characterize the adsorbent after desorption to show that the active sites are still available for more adsorption experiment cycles. The challenge

may have come from the use of acids during desorption which may have affected the organic chelating sites of the adsorbents. Therefore, the use of acids for desorption of metal ions from modified PAN-nfs should be critically optimized. However, alternative regenerant such as EDTA is preferred for the purpose of regeneration of the modified PAN-nfs.

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