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Removal of lead and arsenic ions by a new series of aniline based polyamines

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ABSTRACT

A new series of aniline based polyamines were produced via mannich polycondensation reaction of aniline, formaldehyde and various alkyldiamines. The synthesized polyamines were characterized by solid ^{13}C NMR, FT-IR and elemental analysis. Crystallinity and Surface morphology was investigated by powder X-ray diffraction and SEM-EDX. Thermal stability was tested by thermogravimetric analysis. Adsorption properties toward lead (II) and Arsenic (V) ions was studied by model solutions at controlled conditions (pH, time, temperature and initial concentration). An-Buta polymer showed higher efficacy toward the removal of lead and arsenic ions and was selected to be used in the treatment of wastewater samples and showed efficient removal % of ~99% and % 85 for lead (II) and Arsenic (V) ions respectively. The results reveal the high potential of the synthesized polyamines to be potential adsorbents for wastewater treatment.

1. Introduction

Despite the popular knowledge that over two-thirds of the earth's surface area covered by water, only ~2.5% of this is available as freshwater of which ice caps and glaciers locked up to 69% of it; the need to recycle the limited available water is therefore inevitable as failure to do so poses great health risks. Heavy metals (like lead and arsenic) disposed in water from various human activities, especially industrial, even at trace levels, are of potential threat to animals and ultimately to humans as they are non-biodegradable and bioaccumulation in the human body can cause various diseases and disorders (Postel et al., 1996; Berger and Finkbeiner, 2013; Ali et al., 2013; Sun et al., 2014; Graeme Md and Pollack, 1998). Removal of lead and arsenic is achieved by one or more of the methods like chemical precipitation, adsorption, biosorption, electrodialytic process, ion exchange, ultra-filtration, reverse osmosis, electro-deposition, solvent extraction, foam-flotation, cementation, complexation/sequestration, filtration and evaporation. However, of all these techniques, adsorption is considered the most attractive due to availability of several low-cost, easily accessible and environmentally friendly adsorbents (Denizli et al., 2000; Tao et al., 2009; Al Hamouz and Ali, 2012a).

Lead poisoning is a well-known cause of neurobehavioral-cognitive deficits in children and adolescents (Rosen, 1995). A more recent study shows that early life exposure to lead poses a threat to fetal outcomes at birth and normal fetal growth (Xie et al., 2013). Arsenic, on the other hand, has been associated with skin and internal cancer development in humans; non-carcinogenic effects associated with arsenic are peripheral neuropathy, diabetes, and cardiovascular diseases (Abernathy et al., 1999).

Mannich-type polycondensation reactions with formaldehyde have been reported for production of polymers. Endo and Sudo (2009) described the polymerization of a bifunctional benzoxazine from bisphenol-A and aniline resulting in a phenolic moiety bridged by Mannich-type linkage (-CH_2-NR-CH_2-) (Endo and Sudo, 2009). Altinkok et al. (2011) also used similar monomers but sulfonediamine was used in place of aniline to prepare polybenzoxazine (Altinkok et al., 2011). Baraka et al. (2007) was able to synthesize a new chelating resin from nitrilotriacetic acid (NTA) and melamine using mannich-type reaction and tested it for heavy metal removal from simulated wastewater (Baraka et al., 2007). Evidently, Mannich-type polycondensation reactions have enabled researchers to produce polymers with specific functionalities or a combination of several desired

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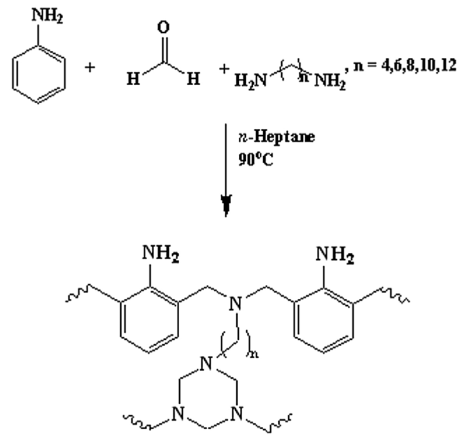

Scheme 1 – Synthesis of novel polyamines.

functionalities for different applications including removal of heavy metals from wastewater (Endo and Sudo, 2009; Baraka et al., 2007; Chutayothin and Ishida, 2010; Singru et al., 2010).

Gurnule et al. (2002) studied the ion-exchange of a salicylic acid–melamine–formaldehyde resin for seven metal ions including Co, Zn, Cu, Ni, Cd, Fe and Pb ions, the removal efficacies ranged from 82% to 97% (Gurnule et al., 2002). Singru et al. (2010) also reported a similar study for the chelating ion-exchange ability of a p-Cresol-melamine terpolymer for these same metal ions with a % removal of 91%–97% (Singru et al., 2010). Liu et al. (2010) functionalized poly (glycidyl methacrylate) (PGMA) beads with four aliphatic amines namely ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) and tested them for adsorption of Cu ions; results showed that the DETA-functionalized polymer was superior in adsorption capacity because of the relatively high amine content with a *Qm* range of 1.0–1.2 mmol g^{-1}(Liu et al., 2010).

Polyaniline, especially, has been one of the most efficient of the chelating ion-exchange polyamines. Recent applications include its use as a component of composites with materials like silica gel, polypyrrole, graphene etc (Ghorbani et al., 2010; Liu et al., 2014). Researchers have even introduced polyaniline coatings on various materials like mesoporous silica, silica gel, jute fiber and saw dust (Ansari and Raofie, 2006; Kumar et al., 2007; Kumar and Chakraborty, 2009; Nayab et al., 2014). However, most of these reports have not explored the potential efficacy of polymers with amine functionality from two different monomers.

In this work, a novel series of polyamines was synthesized and characterized using different spectroscopic techniques for the removal of toxic metal ions. The novel series were tested for their efficacy in the removal of lead (II) and Arsenic (V) from model and real wastewater samples via batch equilibrium studies.

2. Experimental

2.1. Materials and characterization techniques

Aniline (An), paraformaldehyde, 1,4-diaminbutane (Buta), 1,6-diaminohexane (Hexa), 1,8-diaminooctane (Octa),1,10-diaminodecane (Deca) and 1,12-diaminododecane from Fluka Chemie AG (Buchs, Switzerland) were used as received. All solvents used were of analytical grade. Infrared spectra were recorded on a PerkinElmer 16F PC FTIR in the 500–4000 cm^{-1} region (FT-IR). ^{13}C-NMR solid state spectra were recorded on a Bruker WB-400 spectrometer. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (STA 429) by Netzsch (Germany). X-ray analysis was performed on Rigaku Rint D/max-2500 diffractometer using Cu Kα radiation (wave length = 1.5418 A) in a scanning range $2\theta = 5–50°$. Inductively coupled plasma-mass spectroscopy (ICP-MS) analysis was performed using ICP-MS XSERIES-II (Thermo Scientific). Scanning electron microscopy images were taken by TESCAN LYRA 3 (Czech Republic) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector model X-Max.

Table 1 – Mannich condensation terpolymerization[a] of Aniline-formaldehyde-alkyldiamine polymers.

Polyamine	Yield (%)[b]
An-Buta	44.98
An- Hexa	69.49
An-Octa	75.01
An-Deca	76.60
An-Dodeca	80.10

[a] Polymerization reactions were carried out using 0.01 mol of Aniline, 0.03 mol of alkyldiamine and 0.06 mol of paraformaldehyde in 30 ml *n*-heptane at 90 °C for 24 h.
[b] Yield (%) = (mass of product/mass of reactants) × 100%.

Table 2 – % Removal of Lead (II) and Arsenic (V) ions by An-Buta and An-Dodeca, respectively.

Polymer	Metal	Initial concentration, C_o ($\mu g l^{-1}$)	q_e ($\mu g g^{-1}$)	% Removal
An-Buta	Lead (II)	200	103.3	78
		400	255.6	96
		600	388.0	97
		800	523.0	98
		1000	658.7	99
An-Dodeca	Arsenic (V)	200	28.0	19
		400	135.0	36
		600	258.0	55
		800	410.8	77
		1000	557.0	84

2.2. Synthesis of aniline based polyamines

The cross-linked polymers were synthesized via one-pot in situ polymecondensation reaction of aniline (0.01 mol), diaminoalkane (0.03 mol) and paraformaldehyde (0.06 mol) in 30 ml *n*-heptane at 90 °C for 24 h with continuous stirring. Once the reaction completed the resulted product was filtered, washed with distilled water and dried under vacuum at 60 °C until a constant weight is achieved (Table 1).

2.3. Adsorption experiments

Prior to full investigation the polymers synthesized were evaluated in order to determine the most efficient polymer toward the removal of lead and arsenic ion. The most efficient polymer is then further tested as follows: in a typical experiment; 0.03 g polymer sample was inserted in a 20 ml metal ion solution at a specified condition (pH, adsorption time, ion initial concentration and temperature). Once the adsorption experiment completed the solution was filtered and the concentration of metal ions in the filtrate was measured by ICP-MS (Al Hamouz and Ali, 2012b). The adsorption capacity of the polymer toward metal ions (q_e) in mg g^{-1} can be determined by Eq. (1):

$$q_e = \frac{(C_o - C_f)\,V}{W} \tag{1}$$

where C_o and C_f are initial and final concentration of Lead (II) ions in mg l^{-1}, respectively, W is the weight of the dried terpolymer in g, and V is the volume of solution in L.