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Review article

Nanoadsorbents based on conducting polymer nanocomposites with main focus on polyaniline and its derivatives for removal of heavy metal ions/ dyes: A review



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ABSTRACT

Water contamination by toxic heavy metal ions and dyes remains a serious public health problem for humans, so attention on specific methods and technologies to remove heavy metal ions and dyes from wastewaters/aqueous solutions are desired. Numerous adsorbents have been reported for the removal of heavy metal ions/dyes from wastewaters/aqueous solutions. Polyaniline (PANI) and its derivatives, as conducting polymers, are good adsorbents to remove various kinds of heavy metal ions and dyes from wastewaters/aqueous solutions. The nanoadsorbents based on PANI and its derivatives have received much consideration, and are extensively reported in literature. This review focuses on the PANI and its derivatives based on nanoadsorbents for water purification. Various types of these nanoadsorbents used for the removal of heavy metal ions/dyes from wastewaters/aqueous solutions are also briefly compared in this review.

1. Introduction

1.1. The importance of safe drinking water

Water is a vitally important compound for human life. About 60% of the human body is water. Water is also an essential resource for producing food,

clothing, and maintaining our health and environment (Zare et al., 2016), so access to safe drinking water is very important all over the world. The generation of an enormous amount of harmful chemical waste from various industries, and its improper disposal further intensifies the water crisis (Huang et al., 2014). Pollutants can be divided into four categories: physical, chemical, biological and radiological (Bernard and Nebel, 1999).

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Abbreviations: PANI, Polyaniline; As, Arsenic; Hg, Mercury; Cr, Chromium; Pb, Lead; Ni, Nickel; Cd, Cadmium; Co, Cobalt; Cu, Copper; RHS, Rice husk; WS, Walnut shell; OP, Orange peel; SFSS, Sunflower seed shells; ES, Eggshell; SD, Sawdust; PP, Pomegranate peel; CP, Carrot pulp; SB, Soybean; CSH, Cottonseed hulls; OS, Olive Stone; FA, Fly ash; CR, Congo red; IC, Indigo carmine; C.I., Color index; RB, Rhodamine B; AD, Azo dyes; ADAO, Azo dye acid orange; DD, Diazo dye; MB, Methylene blue; MO, Methylene orange; AO, Acid orange; NR, Neutral red; BD, Basic dye; CNTs, Carbon nanotubes; MWCNTs, Multi walled carbon nanotubes; G, Graphene; GO, Graphene oxide; MGO, Malachite green oxalate; RBBR, Remazol brilliant blue R; CD, Cationic dyes; MV, Methyl violet; RB, Rhodamine B; OG, Orange G; RR, Reactive red; RB, Reactive blue; AB, Acid black; COD, Chemical oxygen demand; EY, Eosin Y; HA, Hydroxyapatite; HOMO, Highest occupied molecular orbital; LUMO, Lowest unoccupied molecular orbital; St, Starch; Dex, Dextrin; CL, Cellulose; CS, Chitosan; CB, Conduction band; VB, Valence band; ALG, Alginate; Dext, Dextran; DR, Direct red; DBD, Direct blue dye; RG, Rhodamine G; BV, Basic violet; PACAA, Poly(amidoamine-co-acrylic acid); PSMA, Poly(styrene-altmaleic anhydride); PNVCCMA, Poly(N-vinyl caprolactam-co-maleic acid); PANCS, Poly(acrylonitrile-co-styrene); PAANAF, Poly(anthranilic acid/4-nitroaniline/formaldehyde); PTh, Polythiophene; PEI, Polyethelenamine; PPy, Polypyrrole; RHA, Rice husk ash; MPSAMA, Modified poly(styrene-alt-maleic anhydride); Te, Tenorite; P3MTh, Poly(3-methylthiophene); PPDTh, Poly(3,4-propylenedioxythiophene); CPs, Conductive polymers; DMF, N, N-dimethylformamide; DMSO, Dimethyl sulfoxide; NMP, N-methylpyrrolidone; SDS, Sodium dodecyl sulfate; CTAB, Cetyltri-methylammonium bromide; NPE, Nonylphenol ethoxylate; SAR, Sulfonated acid red; SA, Surfulamic acid; CA, Citric acid; TA, Taurine; TFZB, Thiol-functionalized zeolite Beta; DI, Neutral deionized; PANI-ES, Polyaniline emeraldine salt; PoPDA, Poly(o-phenylenediamine); PProDOT, Poly(3,4-propylenedioxythiophene); APS, Ammonium persulfate; AR, Acidic red; PmPDA, Poly(m-phenylenediamine); PpPDA, Poly(p-phenylenediamine); PVP, Poly(N-vinylpyrrolidone); HM, Hollow microspheres; PANICSP, Poly(aniline-co-m-sulfophenylene diamine); PANICSA, Poly(aniline-co-5-sulfo-2-anisidine); Ani, Aniline; mSPD, m-sulfophenylene diamine; 5S2A, 5-sulfo-2-anisidine; PANDAN, Poly(aniline-co-1,8-diaminonaphthalene); PPy-PANI, Poly(pyrrole-co-aniline); PANOA, Poly(aniline-co-o-aminophenol); pSmPDA, p-sulfonic-m-phenylenediamine; PAMpDA, Poly(aniline-co-m-phenylenediamine); PA3ABA, Poly(aniline-co-3-aminobenzoic acid); PANIGCS, PANI grafted chitosan; CBB, Coomassie brilliant blue; CAc, Cellulose acetate; EPS, Extracellular polymeric substances; LC, Lignocellulose; CALG, Calcium alginate; NMANI, N-methylaniline; NEANI, N-ethylaniline; 2EANI, 2-ethylaniline; PEG, Polyethylene glycol; PS, Polystyrene; PAM, Polyamide; PVA, Polyvinyl alcohol; PET, Poly(ethylene terephthalate); MMS, Magnetic mesoporous silica; TCATS, Thiacalix[4]arene tetrasulfonate; PAmABAmPD, Poly(aniline-co-m-aminobenzoicacidco-m-phenylenediamine); HMS, Hexagonal mesoporous silica; NS, Natural silica; ZSP, Zirconium (IV) silicophosphate; LDHs, Layered double hydroxides; RGO, Reduction graphene oxide; AC, Active carbone; N.R, No reported; PANINTs, Polyaniline nanotubes

- 1. Physical pollutants mainly influence the physical appearance or other physical properties of water (e.g., sediment or material suspended in the water from erosion of soil).
- Chemical pollutants are elements or compounds, which can be naturally occurring or man-made (e.g., bleach, pesticides, metals, drugs, cosmetics, phytosanitary products, insecticides).
- 3. Biological pollutants are microbes or microbiological pollutants (e.g., bacteria, viruses, and parasites).
- Radiological pollutants are chemical elements with unstable atoms that can emit ionizing radiation (e.g., cesium, plutonium and uranium).

1.2. Heavy metals

Heavy metals are elements with atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Fu and Wang, 2011; Srivastava and Majumder, 2008). Nowadays, the heavy metal pollution of wastewater is the most important environmental problem threatening human life throughout the world due to the mobility of these pollutants in natural water ecosystems and their toxicity.

With the rapid development of industries such as mining, metal plating, tanneries, batteries, fertilizers, pesticides and paper industries, heavy metal ions are directly or indirectly discharged into rivers, lakes, or ocean environments (Sud et al., 2008). The heavy metal ions are stable environmental contaminants since they cannot be degraded and destroyed (Demirbas, 2008). Toxic heavy metals ions, such as arsenic, copper, zinc, nickel, cadmium, chromium, mercury and lead can be harmful to water and also remain a serious public health problem.

Some heavy metals, such as copper, zinc, iron, and manganese are vital to the body in very low doses. However, if they are stored in the body in concentrations sufficient to cause poisoning, drastic destruction may occur. The following diseases are examples of poisoning caused by heavy metals (Fu and Wang, 2011; Huang et al., 2014):

Arsenic (As): As can cause lung and skin cancers.

Mercury (Hg): Hg can cause impairment of pulmonary and kidney function, chest pain and dyspnea.

Chromium (Cr): Cr can accumulate in food chain and alter the human physiology. It can cause severe health problems ranging from simple skin irritation to lung cancer.

Lead (Pb): Pb can cause severe dysfunction in the kidneys, liver and reproductive system.

Nickel (Ni): Ni, known as a human carcinogen, can cause dermatitis and allergic sensitization, lung and kidney problems.

Cadmium (Cd): Cd can cause high blood pressure, kidney damage, and destruction of testicular tissue, osteoporosis and destruction of red blood cells.

Cobalt (Co): Co can cause vomiting, nausea, diarrhea, asthma, pneumonia, kidney congestion, skin degeneration and weight loss. **Copper (Cu):** Cu can cause vomiting, diarrhea, stomach cramps, and nausea, or even death.

1.3. Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied (Yagub et al., 2014). Dyes have an aromatic molecular structure, which probably comes from hydrocarbons, such as toluene, benzene, anthracene, naphthalene, xy-lene, etc. (Gong et al., 2005; Gupta et al., 2013). They have two key components: the chromophores, which produce the color, and the auxochromes, which are attached to a chromophore and modify its ability (Gupta and Suhas, 2009).

There are two major types of dyes including natural and synthetic dyes (Karadag et al., 2007; Sharma et al., 2011). The natural dyes are extracted from natural substances, such as plants, animals, or minerals (Vankar, 2000). Synthetic dyes are made in a laboratory and used in the

textile industry (Forgacs et al., 2004; Venkataraman, 1971). They are largely classified as basic, direct, vat, reactive, azoic, sulfur, mordant, acid, disperse, oxidation, mineral, and pigment dyes (Forgacs et al., 2004; Venkataraman, 1971).

In addition to the above-mentioned classification, dyes are also classified based on their particle charge upon dissolution in aqueous medium as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (disperse dyes) (Attia et al., 2006; Hameed et al., 2007; Mall et al., 2006). Much concern has been expressed regarding the use of dyes, due to their reported toxic effects. They can cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity (Srivastava et al., 2004). Therefore, according to the abovementioned diseases resulting from heavy metal ions and dyes, research into the specific methods and technologies to remove heavy metal ions and dyes from wastewater/aqueous solutions is desired.

1.4. Appropriate methods for the removal of heavy metal ions/dyes

Many techniques such as, ion-exchange, physical and chemical precipitation, membrane filtration, electrochemical treatment, reverse osmosis, solvent extraction, and adsorption processes are extensively-used methods for removing heavy metal ions from wastewater/aqueous solutions (Bulut, 2007; Demirbas, 2008).

On the other hand, some approaches such as, chemical oxidation, coagulation, electrochemistry, aerobic and anaerobic microbial degradation, membrane separation, and adsorption have been applied to removing dyes from wastewater/aqueous solutions (Gupta et al., 2013; Malik and Sanyal, 2004).

Among various techniques for removing heavy metal ions and dyes from wastewater/aqueous solutions, adsorption is considered one of the most possible and effective techniques for water treatment (Lakouraj et al., 2014a, 2014b). Adsorption has been found to be superior to other methods in terms of the flexibility and simplicity of design, initial cost, ease of operation and insensitivity to toxic pollutants. In addition, it does not result in the formation of harmful substances (Hua et al., 2012; Rafatullah et al., 2010).

1.4.1. Effective factors on the adsorption of heavy metal ions/dyes

There are many factors affecting the adsorption of heavy metal ions and dyes. These factors include the pH of solution, adsorbent dosage, contact time, concentration of initial heavy metal ions/dyes, and temperature (Yagub et al., 2014; Zare et al., 2016, 2015b). The optimization of these conditions can significantly help in the development of heavy metal ions/dyes removal.

1.4.1.1. pH. The variations in pH can determine the ionization degree of an adsorptive molecule as well as the surface properties of an adsorbent (Nandi et al., 2009; Yagub et al., 2014; Zare et al., 2015b), so the initial pH of a solution is a significant and imperative factor affecting the capacity of an adsorbent in water treatment. Furthermore, the dependence of sorption on pH is associated with both the metal and dye chemistry in the solution and the ionization state of the functional groups of the sorbent (Yagub et al., 2014).

1.4.1.2. Adsorbent dosage. A material which has the capability of adsorbing molecules of gases, liquids, or solids without any physical or chemical change is called an adsorbent (Dąbrowski, 2001). The adsorbent amount is an important factor controlling the adsorbent capacity for a certain amount of an adsorbent at the operating conditions (Zare et al., 2016, 2015b). The removal percentage usually increases as the adsorbent amount increases. In fact, the sorption sites at the adsorbent surface increase by increasing the amount of the adsorbent, so this factor provides an idea for the ability of a metal/dye adsorption to be adsorbed with the minimum amount of the adsorbent (Yagub et al., 2014).

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