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Removal of heavy metals from wastewater by economical polymeric collectors using dissolved air flotation process

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ABSTRACT

Dissolved air flotation (DAF) process has been widely used for many applications including waste water treatment. For the purpose of heavy-metal removal, this study will implement several commercial polymers as collectors in DAF process. The investigated polymers are polyvinyl alcohol, polyethylene glycol, and chitosan which will be used as separation-enhancing agents in the air flotation process. On the other hand, the studied heavy metals are zinc chloride, lead(II) nitrate, manganese(II) chloride, nickel chloride, and cadmium chloride. Different parameters have been studied in this work such as the concentration and types of collectors, modification of polyvinyl alcohol, and the type and concentration of the heavy metals.

The results showed that chitosan was generally better than the other investigated polymers in affecting the removal of Cd (29%), Ni (27%), Mn (31%), and Pb (29%). The removal of Zn was not consistently high for any type of polymers, although it was less with chitosan. Polyvinyl alcohol was modified by carboxylation and the modified polymers were found to be more effective at removing the smaller metals such as Ni (30%), and Zn (28%), and less effective at removing the larger metals Cd (24%) and Pb (29%) at heavy concentration of 250 ppm.

1. Introduction

Wastewater treatment represents one of the main processes for recycling water that compensates the shortage of water in many areas in the world. The facilities that treat wastewater are not enough at the present, only about 10% of the wastewater generated is treated and the remaining is disposed into our water bodies [1]. As such, pollutants enter groundwater, rivers, seas and other water sources. Such water, which ultimately ends up in our households, is often highly contaminated and carries disease-causing microbes. All of these reasons motivate the researchers to investigate different ways to treat wastewater. Heavy metals, at high concentration levels, are the most important contaminants in wastewater, as their presence leads to serious environmental and human problems [2]. For example, Manganese is associated with some neurological disorders such as anger, aggression, inability to inhibit inappropriate responding, and criminality. Nickel was named allergen of the year in 2008 by the American Contact Dermatitis Society (ACDS) [3]. It was also suggested to play a role in breast cancer [4]. Zinc used in antidandruff shampoo was shown to cause allergic contact dermatitis, and high levels of exposure over time can cause brittle hair and nails, as well as neurological abnormalities. Zinc also could cause gastrointestinal disorders and convulsions [5–6]. Cadmium and lead cause damage to the kidneys and severely affect the neurological system [7]. Table 1 shows some types of wastewater produced from some industries and their main heavy metal concentration compared to their standard concentration limits according to the World Health Organization (WHO) [8–12]. As an example, the table shows that lead concentration varies between 2.99 and 7083 mg/l while the standard limit for lead is 5 mg/l.

Several methods were implemented for the removal of heavy metals from wastewater such as filtration, membranes, disinfection, settling, coagulation, flocculation and flotation [11–12,13]. The later method is the most effective method which has been used widely in mineral processing, paper, pulp, food, and wastewater treatment [1,14–19].

The flotation method relies on differences in the surface properties of different particles, specifically wetting characteristics, to separate one particle type from another. The hydrophobic particles escape from water by attaching to air bubbles, which rise to the

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Table 1
Pb, Mn, Zn, Ag levels reported in industrial waste water [8–11].

Source	Heavy metals concentrations in wastewater (mg/l)	Maximum allowable limit (mg/l) [12]
Pb		10
Mining	2.99–7083	
Lead diazide production	1500	
Steel production	20–500	
Mn		0.05
Titanium dioxide production	46	
Mining	410–6700	
Zn		5
Paint manufacturing	0.3–77.4	
Zinc plating	2–1050	
Pigment manufacturing	0–1702	
Metal processing	0.2–1.0	
Textile dying	2–6	
Steel works	2.1–1210	
Ni		0.01
Coating industry	0.0693–0.11	
Cd		0.005
Cadmium–nickel batteries	100–200	
Cadmium plating	100–200	
Mining	0–1	

surface, and are captured in the froth phase. The froth is removed and the concentrate of separated hydrophobic particles is used as is or is sent off for further processing [1].

There are several types of flotation methods such as ion flotation, electrolytic flotation, precipitate flotation, and dissolved air flotation (DAF) [1,20–21]. The latter method is the most effective one as it has an ability to separate light and small suspended solids [22].

Collectors are reagents that are used in the DAF process to selectively adsorb onto the surfaces of particles. Collectors can be either chemisorbed or physically adsorbed [23]. They form a monolayer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons. The collectors greatly increase the contact angle so that bubbles adhere to the surface. Selection of the correct collector is critical for an effective separation by froth flotation. Organic polymer collectors are used in metallurgical waste [20]. They can be characterized by two properties, the molecular weight and the length of polymer chain. These polymers can be classified into low molecular weight (LMW), mid molecular weight (MMW), and high molecular weight (HMW) [24].

Many workers [25–30] used DAF as a treatment process for waste water. Offringa reported that suspended solids of 200 to 300 mg/l in sewage water were successfully reduced to 10 mg/l using DAF [25]. In another study, DAF was investigated to treat wastewater produced in pulp and paper mills [26]. Under proper flocculation conditions, solids removal between 80 and 98% was successfully achieved from feed concentrations of 600 to 6000 mg/l. On the other hand, DAF process was found to be preferred over the sedimentation process in many waste water treatment applications. Tassel et al. [27] studied the removal of mercury from mercury diethyl dithicarbonate using DAF and the settling process. The results showed that DAF was a very good technique in which 98% of solids were removed. In comparison to the settling technique, DAF was more efficient as higher purity and lower turbidity of the product was obtained.

DAF was implemented by other workers to treat surface and seawater [28]. DAF was used as a pretreatment process for spiral-wound module nanofiltration (SWNF) to treat the Tagus River surface water in Valadas, Portugal using aluminum sulphate, ferric chloride, and chitosan as coagulants [29]. With this hybrid system, the silt density index (SDI) value was accepted for the treated surface water. In another work, DAF with ultrafiltration was used as pretreatment for reverse osmosis (RO) performed on open seawater intake at a pilot plant located in the Persian Gulf [30]. In this study, the studied parameters for the water quality characterization were suspended solids, turbidity, fouling tendency, organic matters, and algae content. The filtered water obtained by the pilot plant was very steady, and SDI was below the required value. Based on these promising results, a full industrial plant, a 37.5 MGD open seawater intake desalination plant located in Fujairah, was constructed. However, the previous study did not consider the removal of heavy metals form seawater.

Ferric chloride is the most used coagulant. However, Bunker et al. [31] indicated that the selection of the coagulant should be based on water temperature and raw water characteristics such as particle concentration as well as the type and the concentration and nature of natural organic matter. Klute et al. [32] demonstrated the importance of the optimization of the coagulation process prior to DAF with an extensive investigation of pH effects, coagulant concentration, and mixing and flocculation intensity in a pilot plant. In another study, aluminum and ferric sulphates have been used to remove oil from emulsion solution [33]. However, there are some drawbacks in the application of inorganic coagulation/flocculation to treat wastewater:

(1) It increases the production of inorganic sludge which results in increasing sludge handling costs and a significant amount of remaining ashes after sludge incineration. (2) It causes an increase in the salinity of the effluent due to the release of counter ions by the flocculants. Polymers are effective over a wider pH range than inorganic coagulants. They can be applied at lower doses, and produce smaller volumes of more concentrated, rapidly settling flocculants. The flocculants formed from the use of a properly selected polymer will be more resistant to shear, resulting in less carryover and a cleaner effluent.

Polymers have been utilized in coagulation/flocculation processes for water purification for almost four decades [34]. In comparison with alum, some of the advantages from the use of polymers in water treatment are [35–36]:

1. Lower coagulant dose requirements,
2. A smaller volume of sludge,
3. A smaller increase in the ionic load of the treated water,
4. A reduced level of aluminum in treated water,
5. Cost savings of up to 25–30%.

Synthetic organic polymers used in water treatment are most commonly sold in the form of dry powders or inverse emulsion and are categorized into two major types [37].

(1) Low to mid molecular weight cationic coagulants based on nonquaternised dimethylamine (polyamines) and diallyldimethyl ammonium chlorides (DADMACs); (2) Very high molecular weight polyacrylamides (PAMs) flocculants, which may be anionic, cationic or nonionic.

In this research, different polymers will be investigated as collectors to remove heavy metals from wastewater using DAF process. These polymers are polyvinyl alcohol (PVA), modified PVA, polyethylene glycol (PEG), and chitosan. The heavy metal salts that were used in this work are $CdCl_2$, $ZnCl_2$, $MnCl_2$, $Pb(NO_3)_2$, and $NiCl_2$. Different parameters will also be studied in this work such as the concentration and types of collectors, modification of collectors, and the type and concentration of the investigated heavy metals. Finally, DAF process will be implemented to treat sea water as a real practical application to the flotation process since sea water