An evaluation of toxicity effect on flocculants usage in environmental aspects

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Abstract

Coagulation and flocculation processes are widely used for solid liquid separation. These methods have been applied in several industries such as mineral processing, water treatment, processing of industrial wastes either to produce pure water or dewatering of concentrate over the few decades. Waste waters also generated during mineral processing operations such as leaching. Waste waters should be kept under control as these waste waters may frequently contain reagents and heavy metals which are toxic to living population. Although, the process water is recycled to the plant after flocculation, it is also essential from the standpoint of public health and environmental apprehension to determine whether the polymer flocculants and coagulants in water or in sludge exert an adverse biological effect. It is essential that how the coagulants and flocculants affect their living environment for the living population. Therefore, the effects of polymer flocculants and coagulants on many kinds of organisms have been and still being investigated.

Key words: Flocculation, coagulation, polymer, toxicity of reagents, wastewater

1. Introduction

Inorganic insoluble colloidal particles in nature carry charges on their surfaces. The magnitude of this charge determines the stability of suspension [1]. If the magnitude of surface charge is great, the electrical charge will cause the particles to repel each other. These particles can be settled with the addition of organic or inorganic compounds, called flocculants or coagulants, which neutralize the electrical charges. Therefore, coagulation and flocculation are the aggregating methods providing that the suspended small particles are to be transformed into larger-size flocs from the suspension [2,3].

Coagulants have normally low molecular weight, positively charged compounds that are adsorbed onto the solid particles, effectively neutralizing the overall electrical charge of the particles [4-7]. Hydroxy complexes of multivalent ions are specifically very surface active causing a strong adsorption on solid surfaces and may reverse the sign of the zeta potential [4-6,8]. $Al_2(SO4)_3$, $FeCl_3$, $FeCl_3$, $Fe_2(SO4)_3$, $FeSO_4$ are the most common coagulants.

Polymeric flocculants (often called polyelectrolytes) consist of long-chain molecules with high molecular weights and are characterized by their ionic nature as cationic, anionic and non-ionic. Polymers with negative charges are "anionic," those with positive charges are "cationic," and polymers with no electrical charge are "non-ionic." Synthetic polyelectrolytes include polyacrylamides (PAMS) which can also be in several charge states (cationic, anionic and non-

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ionic) and various cationic products, mainly polyamines. The adsorption of polymers is explained by two mechanisms such as charge neutralization and bridging. Theoretically, the polymeric flocculants may be applied either after destabilizing the suspension by coagulation, i.e. pre-destabilization or without destabilization. However, the polymeric flocculants are known to be more effective in pre-destabilized fine particle suspensions [6,9,10]. They are also cited as being used in clarification of drinking water and industrial applications including waste and sludge clarification, thickening, dewatering, paper manufacture and mining [11]. Cationic PAMS are commonly used in municipal wastewater treatment to improve solids removal during pre-settlement. PAM is also used in flocculants for the clarification of potable water and for the treatment of municipal and industrial effluents.

Although the wastes generated during the mining operations may induce the environmental effects mainly water pollution and stability, there is limited study on the effect of residual flocculants on the environment in the current review of the literature accessed. The aim of this work is to evaluate of toxicity effect on flocculant usage in all environmental aspects. Another aim of this study is to draw attention on the detrimental effects of residual chemicals in the waste water during the mineral processing operations for living rather than water treatment process.

2. Materials and Method

EC_{50}/LC_{50} is often used in ecotoxicology as an indicator of the toxicity of a compound to the environment. The median effective concentration (EC_{50}) is the statistically derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions [12]. In the particular case of LC_{50}, the effect is the death of the targeted population of organism. Thus EC stands for "effect concentration" and LC for "lethal concentration". The material safety data sheet (MSDS) of flocculant should include the LC_{50} and should be provided by the manufacturer.

3. Results and Discussion

3.1. Toxicity of Flocculants and Coagulants

Even though coagulants based on the chemistries are used in some potable water treatment applications, they are toxic to fish and cannot be used in applications involving open water discharge. Mineral coagulants such as alum (hydrated aluminium potassium sulphate) and ferric chloride may also be toxic to animals when consumed due to high concentration of residual aluminium and iron [13]. Alum and other aluminium salts are widely used for sewage dewatering and for removal of algae from drinking water, however they are undesirable for animal feed unless the aluminium is removed [14]. Alkaline iron III hydroxide may also be used as a coagulant but has the same toxicity problems [15].

Acrylamide is known to be a cumulative neurotoxin and carcinogen, and may also cause reproductive damage. It is reported in the literature that residual levels of acrylamide are detected in tap water from treatment plants using polyacrylamide flocculation [16]. Flocculation process has also been applied in the harvesting of microalga biomass [17,18].

Synthetic polymers are very efficient and can be customized to the needs of a particular application. However, the biggest drawback is their shear degradability. Besides, they increase the environmental problems because they are not readily biodegradable and some of their degraded monomers, for instance acrylamide is toxic and demonstrates carcinogenic potential [19,20]. Polyelectrolytes are reported in the literature to have a very low mammalian toxicity and are generally considered to be innocuous materials [21]. Despite flocculants show little or no acute, semiacute or chronic toxicities to animals (rats and dogs) in oral administration, some organisms living in aqua are very sensitive to their toxic effects [22,23].

Toxicity varies with charge type and flocculant chemistry. The cationic polymers are recognized to pose a potentially significant hazard to aquatic life, particularly fish, but this varies with crustaceans [24].

Although most of the aquatic organisms living in sea water are insensitive to non-ionic and anionic flocculants, fishes and Daphnia magna in fresh water are reported to be extremely sensitive to cationic flocculants [23-25].

3.2. Effect concentration and lethal concentration of Flocculants and Coagulants

The toxicity of polyelectrolytes to freshwater organisms varies widely, with reported EC_{50}/LC_{50} values between 0.04->4000 mg/l, depending upon ionic state and the particular organisms concerned (e.g. algae, invertebrates or fish). Cationic polymers are more toxic to aquatic life than anionic or non-ionic polyelectrolytes. As an instance, the median EC_{50}/LC_{50} values for invertebrates and fish are 3.9 and 0.89 mg/l respectively [26]. The varying toxicity from cationic polyelectrolytes is explained by differences in charge density, with toxicity increasing as charge density increases. The non-ionic polymers are considered to be the least toxic. Non-ionic polymers and anionic polymers are thought to be the safest and easiest to use (often being in solid form) in environmentally sensitive situations due to their low toxicity. In spite of these limitations, the EC_{50}/LC_{50} range for cationic products is cited as 1000-2370 mg/l while for anionic products is cited as >1000 mg/l for fish. On the other hand, no data is presented for non-ionic products. Although the marine studies are so few as to negate valid comparison with the freshwater data, it is noted that the marine values are 1-2 orders of magnitude greater than comparable values for freshwater fish which showed median EC_{50}/LC_{50} of 0.89 and 37.2 mg/l for cationic and anionic products respectively.

Toxicities of chemicals should also be tested primarily for human consumption, warm-water species of fish, and for various invertebrates. Companies manufacturing the clarifying chemicals are required to conduct toxicity tests for legal aspects in many countries.

Alum is not appreciably toxic to warm-water goldfish (Carassius auratus), sunfish (Lepomis sp.)

or largemouth bass (Micropterus salmiodes) [27]. It was reported that 1 mg/L or less of Purifloc-31 (Dow Chemical Company, Midland, Michigan) was acutely toxic to rainbow trout (Salmo gairdneri) in 36 hours when tests were conducted in clear water [28]. Biesinger and his co-workers tested three ionic forms of polymer flocculants on rainbow trout, lake trout (Salvelinus namaycush), and three crustaceans: a mysid (Mysis relicta), a copepod (Limnocalanus macrurus) and a cladoceran (Daphnia magna). They concluded that some of the cationic polyelectrolytes tested are particularly toxic at concentrations which could be released into aquatic environments. It was also reported that cationic polymers are more toxic to fish than other ionic forms because of their affinity for the negatively charged surface of fish gills [29].

The surface of fish gills carries a negative charge to which cationic polyelectrolytes are readily to bind due to electrostatic attraction [26]. It is likely that sub-lethal effects and mortality of fish is the result of mechanical suffocation, reduction in oxygen transfer and mucous production on gill surfaces. Impacts on invertebrates are similarly to derive from a similar mechanism (that is, interactions with the surfaces of aquatic organisms).

Aluminium coagulants contain high concentrations of ionic aluminium, the toxic form. Toxicity is very dependent on pH and increases at lower pH. At high values of pH, most aluminium is present in solid form and is not bio-available. The bio-availability and toxicity of aluminium is considered to be little threat of toxicity at pH of 6.5, which is the normal range for natural waters. A review by Spry and Weiner concluded that in low-pH water (i.e. 6-6.5 or less): “both sub-lethal and lethal toxicity of aluminium has been clearly demonstrated in both laboratory and field studies at environmental concentrations” [30].

Sensitivity of native biota to pH and heavy metals is discussed by some researchers [31,32]. They reported that New Zealand biota generally appears to be tolerant to these stressors although there is some evidence of effects in streams receiving mine drainage. Molluscs are identified as potentially sensitive to low pH. The most sensitive organisms to metals were the cladoceran Ceriodaphnia dubia and amphipod Paracalliope fluviatilis, while the mayfly Deleatidium sp. was fairly sensitive. Sensitivity of New Zealand aquatic insect species has not been assessed in specific relation to aluminium. However, from the limited available studies on other metal species, it appears unlikely that any species or groups of key ecological significance will be sensitive to potential toxicants released from treated ponds. Lime stabilisation works would, therefore, tend to increase pH causing to buffer the effects of coagulants on pH, and also reduce aluminium toxicity.

Compared to the investigations in animals or aquatic organisms, only a few reports on the effect of the flocculants on plants have been published [33-36]. The flocculants are not effective on germination and growth of rice, Japanese millet, cucumber, radish, rape, and tomato [34]. However, Kuiuhara and Watanabe reported that some cationic flocculants reduced the germination percentage of Chinese cabbage and radish at an application rate of 2 g/kg dry soil [33].

In the light of their low toxicity, anionic and non-ionic polymers are recognised as the safest to use and would be the most appropriate where a particular receiving environment was regarded as a sensitive location. Sensitivity could be based on a variety of values including ecological (e.g. important native fish stocks), chemical (e.g. high natural acidity), cultural or perceptual.

Cationic polymers are widely recognised as having a high toxicity under laboratory conditions in pure waters. Some researchers use flocculants to remove harmful toxic impurities such as arsenic [20], toxic microcystins [37] from the wastewater, toxic pollutants [38,39] from the tannery wastewater. Researchers have also been investigated an alternative inoffensive chemicals to threat the wastewaters. Liu and his co-workers used lignin sulphonate which has non-toxic character as a new type of natural polymer flocculant to remove COD (chemical oxygen demand) from furfural wastewater [40].

In 1967, the first non-toxic and completely synthetic cationic (positively charged) organic polymer was introduced and accepted by the U.S. Public Health Service for treatment of municipal water supplies [41]. Since then, a wide range of polymers has been developed for use in municipal water and wastewater treatment [15]. These polymers are more commonly used today for water clarification than naturally occurring organic compounds.

Conclusions

Companies manufacturing the clarifying chemicals are required to conduct toxicity tests. Although these tests are usually limited, they do provide information on toxicity, maximum allowable dosages, and whether or not the chemical has been approved by the Food and Drug Administration for human consumption, fisheries, or other uses.

The amount of residual flocculant and their effects on stream life arising from such discharges should also be measured. Other factors that may affect the performance of flocculant systems (e.g. soil pH, rainfall and lime stabilisation) should also be considered. The sensitivity of aquatic species to flocculants plays a major role on the effects of flocculant discharges to the marine environment.

As a result Paracelsus says "All things are poison, only the dose permits something not to be poisonous". Water can be toxic in high doses, snake venom can be medicinal in low doses. There is nothing inherently toxic about man-made chemicals, or non-toxic about natural chemicals.

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