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Heavy Metal Removal from Wastewater by using Liquid Liquid Extraction

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ABSTRACT: Heavy metals are toxic and detrimental water pollutant. Their presence is affected human beings and also animals and vegetation because of it's mobility in aqueous ecosystem, toxicity and non-biodegradability. Removal of heavy metals from the effluent is the major research carried out by researchers in the field of environment. Different methods such as ion exchange, membrane filtration, precipitation, evaporation and adsorption are used for it's removal, extraction process has attracted attention of many researchers because of low cost, design flexibility and high efficiency. In this process we will employ the use of solvent extractant. Our aim will be to extract heavy metals from waste water by liquid liquid extraction. In the removal of heavy metals in wastewater, Extractents are popular and effective. Di-(2-ethylhexyl) phosphoric acids (D2EHPA) one of the most effective media for removing a wide range of contaminants from wastewater. D2EHPA is very versatile and efficient for metal extraction in effluent. Amount of heavy metal in wastewater is estimated before and after treatment with D2EHPA by atomic absorption spectroscopy (AAS) test. Here, our main aim is to target the extraction on copper from wastewater by method of extraction using D2EHPA. Copper is essential element in water for living organisms, but in very small amount. Copper is one of the most valuable and prevalent metals used in the industry so high contents of copper can be found in it effluent discharge from that particular industry.

KEYWORDS: Liquid-Liquid Extraction, Ion Recognition, Toxic Metals, D2EHPA, PC-88A, Extraction, Stripping, Separation

I. INTRODUCTION

Heavy metals are defined as metals with relatively high densities, atomic weights, or atomic numbers. They are define on basis of there field, For example, in metallurgy a heavy metal may be defined on the basis of it's density, whereas in physics the distinguishing criterion would be atomic number, while a chemist would likely be more concerned with it's chemical behavior. The earliest known metals were copper, tin, iron, and precious metals such as silver, gold, and platinum—are heavy metals. From 1809 onwards, light metals, such as aluminum, magnesium, and titanium, were discovered, as well as less well-known metals including

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thallium, gallium, and hafnium. Some metals were either essential nutrients (typically iron, cobalt, and zinc), or relatively harmless (such as ruthenium, silver, and indium), but can be toxic if found in larger amounts or certain forms. Other heavy metals, such as mercury, cadmium and lead are highly poisonous.

Heavy metals are natural components of the Earth's crust. It cannot be degraded or destroyed. To a small extent it enters our bodies via food, drinking water and air. As trace elements, some of the heavy metals (e.g. copper, zinc, selenium) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning can result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or from intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulate. They can enter a water supply by consumer and industrial waste, or even from acidic rain breaking down soils and then releasing heavy metals into streams, lakes, rivers, and groundwater.

II. THEORY

Liquid-liquid extraction (LLE) is also known as Solvent Extraction and Partitioning. It is a method to separate metal compounds, based on their relative solubilities in two different immiscible liquids, usually an organic solvent (non-polar) and water (polar). There is a transfer of one or more species from one liquid into another liquid phase, i.e. from aqueous to organic phase. The transfer of species is driven by chemical potential force, i.e. once the transfer is complete, the overall system of electrons and protons that would make up the solutes and the solvents are in a more stable configuration (lower free energy). The solvent that is enriched in solute(s) is called as extract. The feed solution which is depleted in solute(s) is called as raffinate. LLE is the basic technique that is used in chemical laboratories, where it is performed by using a variety of apparatus, from separatory funnels to counter current distribution equipment called as mixer settlers. This type of processes are commonly performed after a chemical reaction to be part of the work-up, including an acidic work-up. The term Partitioning is used to refer to the underlying physical and chemical processes involved in liquid-liquid extraction, but on another reading may be fully synonymous with it. The term solvent extraction can be also referred as the separation of a substance from a mixture by dissolving that substance in a suitable solvent. In that case, a soluble compound is separated from an insoluble complex matrix.

From a hydrometallurgical perspective, solvent extraction is exclusively used in separation and purification of uranium and plutonium, zirconium and hafnium, separation of cobalt and nickel, separation and purification of rare earth elements etc., its greatest advantage being its ability to selectively separate out even very similar metals. One obtains high-purity single metal streams on 'stripping' out the metal value from the 'loaded' organic wherein one can precipitate or deposit the metal value. Stripping is the opposite of extraction i.e. Transfer of mass from organic to aqueous phase. LLE is also widely used in the production of fine organic compounds, the processing of perfumes, the production of vegetable oils and biodiesel, and other industries. It is among the most common initial separation techniques, though some difficulties result in extracting related functional groups.

Liquid-liquid extraction is possible in non-aqueous systems, i.e. In a system consisting of a molten metal in contact with molten salts, metals can be extracted from one phase to the other. This is related to a mercury electrode where a metal can be reduced, the metal will often then dissolve in the mercury to form an amalgam that modifies its electrochemistry greatly. For example, it is possible for sodium cations to be reduced at a mercury cathode to form sodium amalgam, while at an inert electrode (such as platinum) the sodium cations are not reduced. Instead, water is reduced to hydrogen. A detergent or fine solid can be used to stabilize an emulsion, or third phase. In solvent extraction, a distribution ratio is often shown as the measure of how well-extracted a species is. The distribution ratio (K_d) is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, and a large number of other parameters. Here, D is related to the ΔG of the extraction process.

Sometimes, the distribution ratio is referred to the partition coefficient, which is often expressed as the logarithm. In

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solvent extraction, two immiscible liquids are shaken together. The more polar solutes dissolve in the more polar solvent, and the less polar solutes in the less polar solvent. Although the distribution ratio and partition coefficient are often used synonymously. Solute may exist in more than one form in any particular phase, means the partition coefficient (K_d) and distribution ratio (D) will have different values. This is an important distinction to make as whilst the partition coefficient has a fixed value for the partitioning of a solute between two phases, the distribution ratio changes with differing solvent conditions. After performing liquid–liquid extraction, a quantitative measure must be taken to determine the ratio of the solution's total concentration in each phase of the extraction. This quantitative measure is known as the distribution ratio or distribution coefficient.

Success of liquid–liquid extraction is measured through factors of separation and decontamination. The best way to understand the success of an extraction column is through the liquid–liquid equilibrium (LLE) data set. The data set can then be converted into a curve to determine the steady state partitioning behavior of the solute between the two phases. The y-axis is the concentration of solute in the extract (solvent) phase, and the x-axis is the concentration of the solute in the raffinate phase. From here, one can determine steps for the process optimization.

III. HEALTH EFFECTS OF COPPER

Long-term exposure to copper can cause irritation of the eyes, mouth and nose and it cause headaches, dizziness, vomiting stomachaches, and diarrhea. Intentionally high uptakes of copper can cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. There are scientific articles that indicates a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. This should be of concern is a topic for further investigation. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, renal disease, brain damage, demyelization, and copper deposition in the cornea.

IV. ENVIRONMENTAL EFFECTS OF COPPER

When copper ends up in soil it is strongly attached to organic matter and minerals. As a result it travels very less after release and it hardly ever enters groundwater. In surface water copper travels a great distances, either suspended on sludge particles or as free ions. Copper does not break down into the environment and because of that it would accumulate in plants and animals where it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. This is the reason why there is not much plant diversity near copper-disposing factories. Due to the effects of copper upon plants, this is a serious threat to the productions of farmlands. Copper can cause serious influence on the proceedings of certain farmlands, depending upon their acidity of the soil and the presence of organic matter. Despite of this, copper-containing manure is still applied. Copper can interrupt many activities in soils, as it negatively influences the activities of microorganisms and earthworms. The decomposition of organic matter would seriously slow down because of this. When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Mainly sheep suffers great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations.

V. EXPERIMENT WORK

Take 100 ml of wastewater. Make 1N NaOH solution for pH adjustment of waste. Adjust the pH of wastewater from 3 to 5 by adding NaOH solution or HCL. Prepare the mixture of Toluene(90 ml) and Di-2-ethyl Hexyl Phosphoric Acid(10 ml) (Toluene as organic phase and D2EHPA as extractant). Mix this solution with waste effluent by 1:1 ratio. Stirr this mixture for 15-20 minutes. After stirring procedure there will be a separation of aqueous phase and organic phase. Separate these phases in separate beakers by using separating funnel. Measure the pH of aqueous phase and maintain it between 3-5. Again mix the aqueous and organic phase and repeat the procedure until the constant pH has

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been achieved. The organic solution turns into blue colour from colourless as it extracts the copper from wastewater. Add Oxalic acid (as stripping agent) to extract the copper from organic phase. After adding stripping agent, precipitation will occur. These precipitates settles down and being separated through Centrifuge. After centrifuge, backwash of precipitates is to be done by distilled water. This separated Copper compound is Calcinated in Muffle Furnace at 400 ° C for 2 hours. After the calcination, the final product would be Copper Oxide that can be utilize as a catalyst.

VI. RESULTS

The result obtained from the project was that Copper Oxide is formed. Copper oxide content is around 46% obtained through atomic absorption spectroscopy test. Following is result analysis obtained by AAS test (The results are diluted 5 times and then analysed):

Sr no.	Name of sample	Unit	Results (copper)
01	Oxalic acid	ppm	43.4083
02	Re-washed Liquor	ppm	22.9177
03	Stripped Liquor	ppm	110.1942
04	Solid Sample	%	46.89
05	Aq. Phase	ppm	1.4004
06	Wastewater	ppm	0.0784

VII. CONCLUSION

Solvent extraction of copper from aqueous solution was carried out using D2EHPA as extraction. The extraction efficiency of copper 65% was extracted with the help of 10ml D2EHPA in to toluene solution in short of 15-20min. The maximum extraction efficiency was obtained at 3-5 pH. The A/O ration 1:1 is maintained in this study. Stripping reaction was completed within 5min and 60% of the copper was stripped from loaded organic phase. Under optimized condition industrial wastewater was tested and result was found to be satisfactory.

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