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Review on Strategies for Pb and Hg Removal in Floodwaters: The Case of Guilin, Guangxi

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Abstract:

Since 12th June 2024, severe precipitation has struck Guilin due to the long-term intersection of cold and warm air streams. Cutting clean water supplies and sanitation services is detrimental and may threaten citizens' health. Additionally, mercury ions and lead ions are abundant while hard to remove. In this review, different methods of water treatment process in removing heavy metal ions were discussed including chemical precipitation, photocatalysis, and biosorption. Eventually, these methods should be further improved.

Keywords: Flooding; heavy metals; chemical precipitation; photocatalysis; biosorption

1. Introduction

1.1 Introduction to flooding in Guilin

Significant environmental pollution can be brought about by flooding. The movement of floodwaters carries contaminants over extensive areas, resulting in long-term environmental damage. According to the report by Tencent News, although dams were constructed in the upper stream, due to the unexpected rainfall and issues associated with the decision made by the central government, reservoirs could not store water further. On 19th June, the water level in Guilin reached 148.55 meters, which was 2.55 higher than predictions made by the Guilin government, causing waterlogging in urban regions; the flow of floods reached 6100 cubic meters per second. On 20th June, at eight o'clock, the water level started to retreat slowly, reaching 145.99 meters, which was 0.01 meters lower than the alarming line, helping the

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government to clean sludge on streets, divert accumulated water away, and enforce epidemic prevention measures. Although the floods began to retreat after a short period, they still brought tremendous trouble for nearly eight days.

1.2 Aim and significance of this research

The cut of clean water supplies may threaten people's health and influence agricultural outputs and the maintenance of pastures. Thus, restoring the quality of water resources is crucial, turning them into usable or drinkable water. Heavy metals are important pollutants in the flood water. They come from paints from buildings, wastes in factories, and materials in electricity power plants. It is essential to find a way to remove the heavy metal in the water efficiently. In previous cases of urban flooding, mercury and lead ions are abundant while hard to remove due to their characteristics of soft metals. If the concentration of mercury ions and lead ions exceeds the regulated value, besides contamination, damage to people's nervous system, skin, eyes, muscles, kidneys, brain, and liver will occur.[1] In this review, different methods of water treatment process in removing heavy metal ions were compared including chemical precipitation, photocatalysis, and biosorption.

2. Method & Experiment

2.1 Chemical Precipitation

2.1.1 Mechanism

When performing chemical precipitation, reagents are added to water samples, forming insoluble precipitates with metal ions and thus allowing filtration [1]. In general, chemical precipitation can be divided into four phases: supersaturation, nucleation, crystallization, and aging. When excessive chemicals are added to the solution, dissolved matter surges, causing the solution to become supersaturated. To dissipate the excess energy and return to the equilibrium, the formation of solids, the nucleation, is facilitated, bringing the system from a high-energy state to a low-energy state.

$$DF = \frac{C}{C_{saturation}}$$

Where the value of DF is 1.0, the solution is saturated

After the nuclei are formed, crystallization occurs to further mitigate the supersaturated state of the solution. Additionally, since the formation of new solids is more endothermic than attaching to existing nuclei, a crystallization structure will grow.

$$\frac{dC}{dt} = -k \times s \times (C - C_{saturation})$$

Where k is the rate coefficient; and s is the crystal surface area

Eventually, small crystals will dissolve and re-deposit into larger particles with lower solubility, known as aging or ripening [2].

2.1.2 Reagents

Hydroxide precipitation is known for its low cost, simple technique, and easily controlled PH value.

$$M^{2+} + 2(OH)^{-} \rightarrow M(OH)_2$$

Sulfide precipitation is known for the low solubility of precipitates and efficient metal removal at a wide pH range.

$$M^{2+} + S^{-} \rightarrow MS$$

$BDETH_2$ is known for its effectiveness in removing soft metals including lead and mercury from water samples.

$$C_{12}H_{16}N_2O_2S_2 + M^{2+} + 2H_2O \rightarrow C_{12}H_{14}N_2O_2S_2M \downarrow + 2H_3O^{+}$$

[2]

Comparing sulfide precipitation with hydroxide precipitation, sulfide precipitation possesses stronger advantages when removing lead and mercury from water samples. Based on the HSAB principle, soft acids such as lead and mercury tend to form bonds with soft bases such as sulfide ions instead of hard bases including hydroxide ions. Additionally, other heavy metals, acting as hard bases, such as copper and iron may be present. Thus, if hydroxide precipitation is applied, the goal of removing lead and mercury may not be fulfilled [3-4].

The major issue of applying sulfide precipitation is overdose, creating odor and making the water sample toxic. However, the drawback of sulfide precipitation can be mitigated due to the presence of other heavy metals. When treating wastewater and after sulfide ion combines with soft metals, the extra dosage of sulfide ions will react with other hard metals instead of remaining in the water sample. Moreover, precipitants formed after sulfide precipitation are highly insoluble and can adapt to wider pH ranges. On the contrary, lead hydroxide is amphoteric, having strict requirements on the pH value of the water environment when performing the treatment process.

Comparing sulfide precipitation with precipitation using $BDETH_2$, the synthesis of $BDETH_2$ is complex and expensive because this process requires isophthaloyl dichloride, cysteamine, triethylamine, and dry HHPLC-grade chloroform. Additionally, sulfide precipitation is more effective in removing lead and mercury while not requiring a long time for manipulation. When applying $BDETH_2$ to remove lead and mercury, it takes 20 hours to remove lead ions and mercury ions in water samples [2], while it only requires twelve minutes to remove over 99% of lead and mercury ions in water samples when applying sulfide precipitation [2-4].

2.1.3 Experiment

An experiment done by Matlock, M. M., Howerton, B. S., & Atwood, D. A. was cited to validate the effectiveness of chemical precipitation in removing soft metals and hard metals when overdosed while showcasing steps when applying chemical precipitation in water treatment processes. The result of this experiment concluded that the concentration of mercury and lead ions could be reduced to values under 0.37 milligrams per liter. [4].

2.2 Photocatalysis

The term "photocatalysis" combines the words "photo," referring to light, and "catalysis," the acceleration of reactions through providing alternative reaction pathways. The photocatalyst would alter the reaction rate after absorbing energy from photons [5].

2.2.1 Mechanism

The band structure of conductors in solid-state physics contains a valence band and conduction band. The valence band represents the highest electron energy level in a solid where electrons are normally present at 0 Kelvin. Electrons in the valence band are bound to atoms and would function as chemical bonding happens. Valence band is the band of energy levels that electrons occupy before being excited to the conduction band, where electrons are free to move within the material and could conduct electric current. To jump one band to another, electrons must cross the energy difference between the upper limit of valence band and the lower limit of conduction band.

Photocatalysts are typically semiconductors. Semiconductors have a unique band structure: a valence band filled with electrons which are immobile, and a conduction band that is empty. When the catalyst is exposed to light whose photons carry energy no less than the band gap, photons are absorbed and the energy excites electrons to move to the conduction band. This "jump" leaves in the valence band positively charged vacancies (h^+), or holes. The simultaneous presence of electrons (e^-) in the conduction band constitutes electron-hole pairs, which, upon formation, will migrate to the substance's surface and engage in reduction or oxidation. For example, electrons can reduce oxygen to Reactive Oxygen Species (ROS):

$$O_2 + e^- \rightarrow \bullet O_2^-$$

And the ROS could further oxidize pollutants. These electrons could also directly reduce heavy metal ions:

$$Pb^{2+} + 2e^- \rightarrow Pb^0$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \ [6]$$

As a result, harmful heavy metal ions are either reduced to a harmless state or become precipitation.

Meanwhile, the holes (h^+) can participate in oxidation reactions, such as the oxidation of water molecules to corresponding radicals:

$$H_2O + h^+ \rightarrow \bullet OH + H^+$$

Hydroxyl radicals are a typical oxidizing agent that is capable of breaking down organic pollutants and also transforming heavy metal ions into nontoxic forms. The holes can also directly oxidize heavy metal ions. For instance, Pb^{2+} ions can react with holes to form PbO_2:

$$Pb^{2+} + 2h^+ \rightarrow PbO_2 \ [7]$$

In conclusion, photocatalysis utilizes light energy to create reactive electron-hole pairs, which then induce the reduction and oxidation reactions necessary to transform heavy metal ions into solid or nontoxic forms.

2.2.2 Experiments

Multiple laboratory experiments have corroborated the fact that photocatalysis is an effective treatment for heavy metal ions pollutants. Kanakaraju and colleagues conducted an experiment using Titanium Dioxide based photocatalytic beads to remove Cr^{3+}, Cu^{2+}, and Pb^{2+} ions from water. They designed a new photocatalytic material that can be recollected and recycled due to its magnetic properties and investigated the optimal environment conditions for the heavy metal ion removal process. Their research showed that under ultraviolet irradiation at 254 nm, the beads achieved nearly complete removal (> 98.4%) of all three metal ions after 72 minutes of light exposure when the pH value of the surroundings was 6.8 [8]. Three consecutive test cycles which were further conducted to evaluate the stability of the beads demonstrated that a discernible drop in efficiency was not observed after the photocatalyst had been recycled and reused [8].

Y. Xiao's research group focused on a system that uses $CeO_2 / BiOIO_3$ heterojunctions to remove mercury from gaseous environments. They evaluated the heavy metal removal performance of the $CeO_2 / BiOIO_3$ composites when exposed to visible light irradiation. Results showed that the introduction of CeO_2 with $BiOIO_3$ significantly reduced the band gap, and thus made the absorption of visible sunlight more efficient. Specifically, the photocatalytic mercury removal efficiency of the $CeO_2 / BiOIO_3$ heterojunction reached 86.53%, proving the photocata-

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lyst's effectiveness [9].

2.2.3 Limitations in Practical Applications

One primary challenge is the presence of interfering substances within the wastewater matrix that can significantly reduce the efficiency of photocatalysis.

Carbonate species are common in natural waters.

They would act as scavengers of ROS, reducing the number of radicals that could transform toxic heavy metal ions [10]. For example, they readily react with hydroxyl radicals to form carbonate radicals:

$$HCO_3^- + \bullet OH \rightarrow \bullet CO_3^{2-} + H_2O$$

The carbonate radicals formed are generally less reactive than hydroxyl radicals, which diminishes the overall oxidizing power of the photocatalytic system.

Moreover, Natural Organic Matters (NOMs) present in flood-contaminated waters can also hinder photocatalytic efficiency. NOM can absorb a substantial amount of the incident light energy and become excited, which competes with the photocatalyst for photons and reduces the total light energy absorbed by the catalyst:

$$NOM + hv \rightarrow NOM^*$$

Where hv represents the light energy absorbed. Such a reduction in the percentage of activated photocatalyst will lower the number of electron-hole pairs, abating the effectiveness of this treatment [11].

2.3 Biosorption

The mechanisms of biosorption can be divided into two kinds depending on whether it is metabolism-independent.

2.3.1 Biosorption process(metabolism-independent)

The biosorption process is the passive biosorption of dead microbial cell walls, which proceeds rapidly. Also, the biological materials used as biosorbents include algae, fungi, bacteria, and yeast, because these materials possess functional groups such as carboxyl, hydroxyl, and amino on their surface[12][13].

Physical adsorption: Come up due to the van der Waals' forces. In 1988, Kuyucak and Volesky hypothesized that cadmium, zinc, and copper are absorbed by dead biomasses through electrostatic attractions between the metal ions and microbial cell walls[12][13].

Ion exchange: Due to the presence of polysaccharides and bivalent metal ions in the cell walls of microorganisms, they have the capability to exchange these with the anions of the polysaccharides. In particular, biosorption refers to the attachment of metal cations to unoccupied sites rather than those previously held by another cation[12][13].

Precipitation: For precipitation that is independent of cellular metabolism, it could result from the interaction between the metal and the cell membrane. The precipitation caused by metal uptake can occur in both the solution and on the cell surface [12][13].

2.3.2 Bioaccumulation process(metabolism-dependent)

Bioaccumulation is an intracellular process reliant on metabolism, involving the uptake of metal ions by living microorganisms. This process occurs at a slower rate than biosorption. The toxicity of solutions can influence the absorption of metals by living cells, yet in certain cases, significant metal accumulation still occurs. Although this method is generally preferable to biosorption, it can be inhibited by low temperatures.

Complexation: Metals are also removed through the formation of complexes on the cell surface following the reaction between metal ions and the active groups present on the cell wall. These groups include carboxyl, amino, thiol, hydroxy, phosphate, and hydroxy-carboxyl, which can interact in a coordinated manner with heavy metal ions. Furthermore, complexation has been identified as the sole mechanism responsible for the accumulation of calcium, magnesium, cadmium, zinc, copper, and mercury by Pseudomonas syringae[12-15].

Precipitation: The precipitation that occurs as a result of the reaction between target metal(s) and compound(s) takes place during a metabolism-dependent process. This phenomenon is consistently linked to an active defense mechanism employed by microorganisms to safeguard themselves against toxic metals [12][13].

Biosorption typically refers to the capability of inactive, dead microbial biomass to accumulate and bind heavy metals. In this process, biomass functions similarly to a chemical substance, serving as a biological ion exchanger.

2.3.3 Both Biosorption process and Bioaccumulation process

Transport across microbial cell wall: Due to the ability of various cations to diffuse through cell walls and into cells, heavy metals can be translocated across microbial cell membranes via intracellular accumulation. The biosorption process in living organisms occurs in two phases: initially, metals adhere to cell walls without relying on metabolic activities; subsequently, metal ions are absorbed intracellularly in a manner that depends on metabolism, facilitated by transport across the cell membrane [12][13].

2.3.4 Experiment

An experiment conducted by Ascolor Biotec and Ivax Pharmaceuticals proposed that industrial waste biomass can effectively be utilized for the adsorption of heavy metals, specifically lead (Pb) and mercury (Hg). Following a strong alkaline treatment, this biomass proved to be an efficient sorbent for mercury removal from neutral solutions, achieving a maximum uptake capacity nearing 270 mg of mercury per gram. The optimal pH for absorption was identified at an initial value around 5. However, when the pH increased to 6.5, there was no corresponding rise in sorption rates. Moreover, fluctuations in pH levels were found to facilitate the recovery of metals, regardless of the specific metal involved[12-16].

3. Discussion

The method capable of treating the wastewater generated in Gui Lin should fulfill the following requirements: First and most importantly, since the water level in areas of Gui Lin reached as high as 148.8 meters (2), it would be meaningless if the method could only process a small part of the water and leaving the rest of the water polluted, the method should be able to treat wastewater of large quantity; Second, since there are lots of water to be treated, the method should be cost-effective; Thirdly, it should create least secondary pollution as possible. If not, at least there should be economical ways to treat the contaminants; Finally, it should have the ability to remove the Hg and Pb ions to an extent that's above the standard given by WHO.

3.1 Chemical precipitation

As discussed before, this method has limitations regarding the concentration of heavy metals in the wastewater. That is, when the concentration is above 100mg/L, it can only reduce the concentration to 0.2mg/L [17], higher than the standard concentration of 0.01mg/L (WHO). Regarding the cost, the main source of the cost comes from the chemical, or sulfide source, added to the wastewater including H_2S and Na_2S. extra price may come from treating the contaminants since sulfide precipitation does create toxic sludge.

3.2 Photocatalysis

Photocatalysis requires no other energy sources except for light, and Photocatalysts can be recycled in magnetic, all this means this method is quite environmentally friendly. However, the effect of photocatalysts is extremely unstable, especially in the case of the flood in Gui Lin: photocatalysts rely heavily on UV in the sunlight, and it is unrealistic to expect the weather to provide sufficient sunlight for such a long time; what's more, with other variable staying the same, the best pH for photocatalysts to take place is around 4~6[18], while the pH of flood water is usually 6.5~8.5, further weakening photocatalysts' effect. Photocatalysis has other limitations. Presence of interfering substances such as bicarbonates and carbonates within the wastewater matrix that can significantly reduce the efficiency of photocatalysis. Moreover, Natural Organic Matters (NOMs) present in flood-contaminated waters can also hinder photocatalytic efficiency.

3.3 Biosorption

Biosorption fulfills the requirement of being cheap and environmentally friendly. This is because biosorbents are made from abundant or waste material, and it produces no sludge[19], which makes it more environmentally friendly. However, its problem persists in that its capacity is rather limited, and though biosorbents could be reused, it could be time and energy-consuming to take the metal out and reuse it again. As a result, biosorption might have problem processing waste water so much as a flood can generate.

4. Conclusion

As argued, all three methods mentioned above have their drawbacks. Additionally, another limitation is that the composition of floodwater varies in different scenarios because the discrepancy will lead to differences in treatment efficiency. A method that could be widely used in reducing heavy metals in flood water-generated wastewater is desired, and these limitations pose great challenges. In conclusion, the future research direction should focus on improving these methods, such as reducing sludge production and even combining the methods. A hybrid of high efficiency and the scalability of the chemical precipitation and the environmental benefits of biosorption and photocatalysis might be the ideal method. For example, treat heavy metal ions by adding chemical inputs, and address the sludges by employing photocatalysis. It is also plausible to combine two methods to ensure compliance with WHO standards for heavy metal concentration.

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