Applied Chemical Engineering (2023) Volume 6 Issue 3
doi: 10.24294/ace.v6i3.2364

REVIEW ARTICLE

PEG as versatile mediating agent for sensing heavy metal ions: A mini review

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ABSTRACT

The increasing presence of heavy metal ions in aquatic environments has become a subject of escalating concern in contemporary times. Numerous human-induced activities have contributed to an elevated presence of heavy metal ions in aquatic environments, surpassing the threshold levels established by the World Health Organisation (WHO). Recently, there has been a significant increase in the utilisation of polyethylene glycol (PEG) due to its exceptional characteristics in addressing the pressing issue of aquatic pollution resulting from the presence of heavy metal ions. This mini review evaluates the detection activities in which PEG plays a significant role. The detection strategy utilising PEG composites is thoroughly described, beginning with an examination of the inherent properties of PEG. Furthermore, it concludes with suggestions for future research in this area.

Keywords: functionalization; PEG; heavy metal; detection; selectivity

ARTICLE INFO

Received: 4 July 2023
Accepted: 24 August 2023
Available online: 20 October 2023

1. Introduction

Polyethylene glycol is widely regarded as a remarkable substance. PEG has gained significant recognition as a highly esteemed biomaterial due to its extensive range of applications in heavy metal ion sensing as well as their removal[1,2]. PEG possesses several noteworthy attributes, including its ability to undergo biodegradation, its compatibility with biological systems, and its reduced propensity for chemical toxicity[3,4]. Moreover, PEG possesses antibacterial, antifungal, and anti-inflammatory properties, making it a crucial component in the development of therapeutic and diagnostic applications[5,6]. Setting aside all these characteristics, PEG has extensively positioned itself as a suitable agent for sensing applications[7–10]. Recently, researchers had extensively utilised conjugates of PEG to effectively sense aquatic pollutants in the form of heavy metal ions such as arsenic, mercury, etc.[10–12]. While there exist substantial research literatures exploring various properties associated with PEG, it is worth noting that the specific areas of PEG detection in the context of aquatic pollutants have not been adequately addressed in scholarly papers. As such, there is an imminent need for a comprehensive overview that can provide readers with a concise and targeted insight into the recent research endeavours being conducted in this domain.

The paucity of existing literature serves as a motivation for us to write a concise review on PEG, a material that has garnered significant attention. This present mini review aims to examine the sensing properties facilitated by PEG in order to evaluate the concentrations of heavy metal ions. In addition, this study also outlines the procedural details for sensing heavy metal ions and other related aquatic pollutants by utilising PEG-conjugates. This review is anticipated to fulfil a unique objective of providing valuable information to researchers regarding the identification of increasing levels of aquatic pollutants. It delineates the process of detecting aquatic pollutants, specifically heavy metal ions, by employing PEG-mediated agents. Additionally, recommendations for future research in this emerging field are also highlighted.

2. Properties of PEG

Polyethylene glycols (PEGs) encompass a group of linear polymers that are synthesised through a condensation reaction catalysed by a base (see **Figure 1**). This reaction involves the sequential addition of ethylene oxide units to ethylene, resulting in the formation of PEGs. The molecular formula can be represented as (C_2H_4O) mult H_2O, where the term "mult" indicates the average quantity of oxyethylene groups present. The molecular weight can vary within a range of 200 to several million, depending on the quantity of oxyethylene groups present. The materials with higher molecular weights, ranging from 100,000 to 5,000,000, are commonly known as polyethylene oxides[13–15]. The molecular weight of a given polyethylene glycol product typically exhibits a relatively limited range, with a tolerance of approximately ±5%. The nomenclature of specific polyethylene glycols is commonly designated by the number of ethylene oxide units or their approximate molecular weight, such as PEG-4 or PEG-200. Polyethylene glycols (PEGs) with a molecular weight below 600 exhibit a liquid state, while PEGs with a molecular weight of 1000 and higher display a solid state. The substances possess the characteristics of being non-volatile, soluble in water, lacking taste, and lacking odour. The substance exhibits miscibility with water, alcohols, esters, ketones, aromatic solvents, and chlorinated hydrocarbons, while demonstrating immiscibility with alkanes, paraffins, waxes, and ethers[16]. Because of its exquisite properties, it is used in myriad of application as depicted in **Figure 2**.

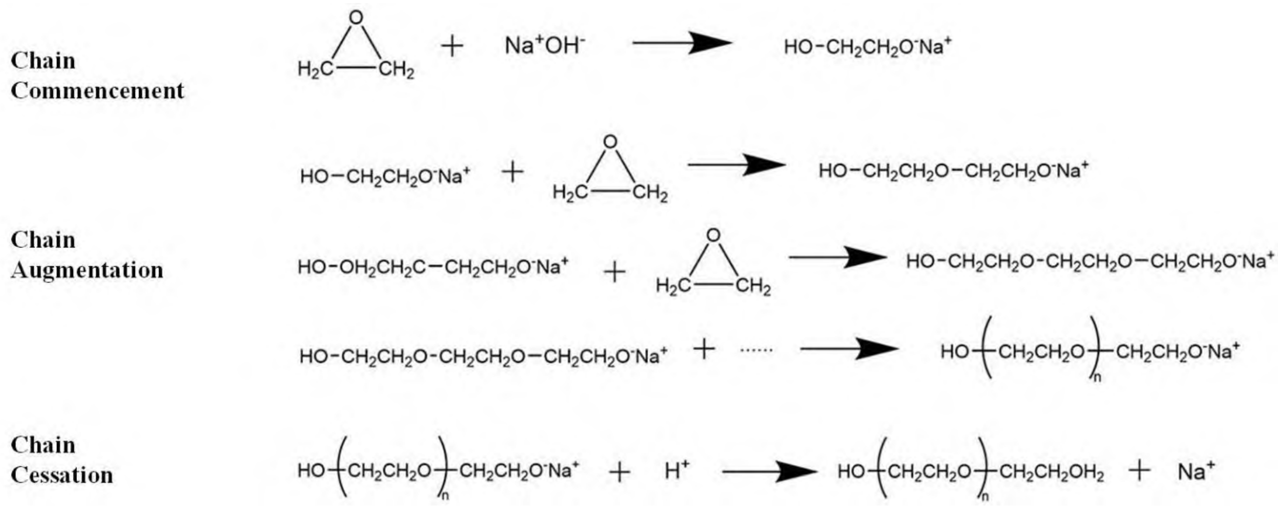

Figure 1. Schematic of anionic polymerization (modified after BOC Sciences[13]).

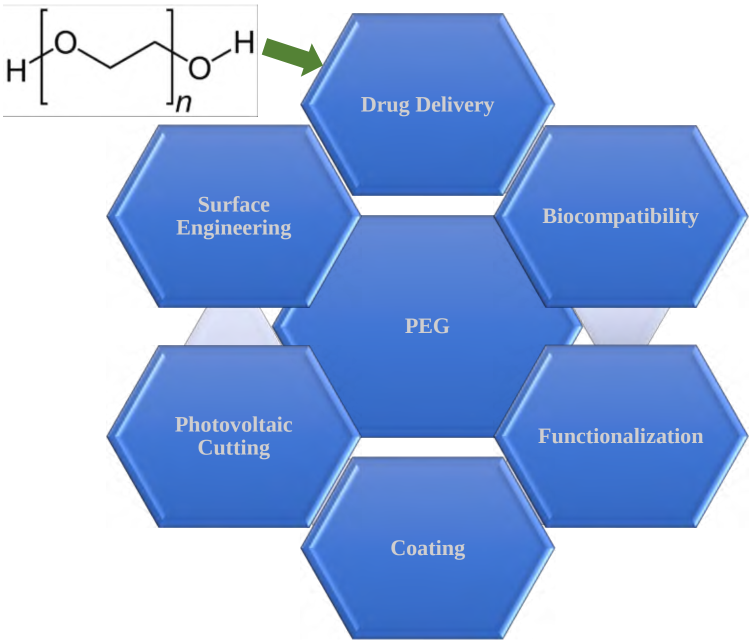

Figure 2. Versatility of Polyethylene glycol (PEG). Inset shows the configuration of PEG.

3. Heavy metal as aquatic pollutants

The issue of water pollution resulting from the toxicity of heavy metals is widely recognised as a significant concern for the environment and ecological systems[17,18]. Water is a fundamental component of all biological systems. The water commonly encountered in our everyday experiences can be classified into two categories: surface water and ground water. Various heavy metals, including lead, zinc, nickel, arsenic, copper, and iron, are present in varying concentrations[19–21]. Certain components are imperative for the sustenance of the metabolic processes within the human organism[22]. These metals are commonly referred to as heavy metal ions due to their relatively high density and toxicity, even at extremely low concentrations[23–25]. Heavy metals have the potential to be introduced into the environment through both natural and anthropogenic sources[26,27]. The sources attributed to human activities include the utilisation of pesticides and herbicides in paddy fields, as well as the industrial application of arsenic compounds, such as in semiconductor technology where arsenic is employed as a doping element[28–30] (See **Figure 3**). These entities are inherently resistant to degradation or destruction. Heavy metals pose a significant hazard due to their propensity for bioaccumulation.

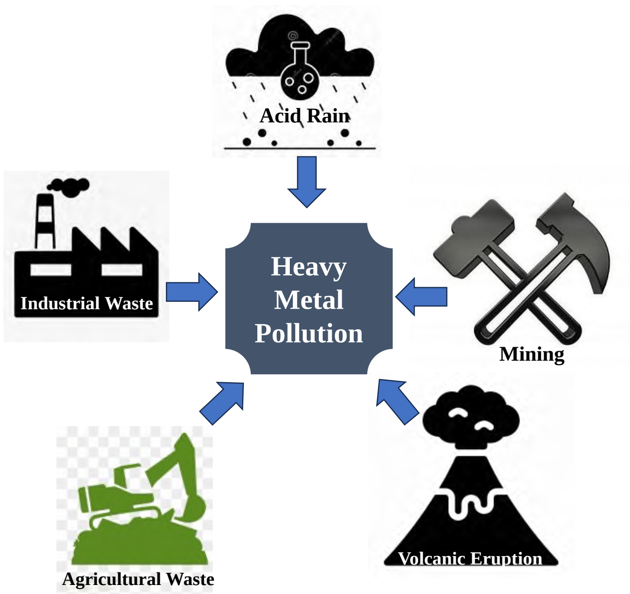

Figure 3. Contributing factors of heavy metal ion pollution of water bodies.

The consumption of water contaminated with heavy metal ions has been associated with a range of health issues, including respiratory, dermatological, urological, hepatic, renal, metabolic, cardiovascular, and nephrological conditions in the human body[20,21]. The heavy metals mercury, cadmium, arsenic, and lead are widely recognised as the four most hazardous pollutants. Mercury is a heavy metal ion known for its toxic properties, and it can exist in both organic and inorganic forms. The stability of mercury in its organic form is attributed to the conversion of inorganic species into organic species via biological processes. Methyl mercury (MeHg) is considered toxic due to its ability to traverse the blood-brain barrier, ultimately resulting in cerebral harm[6]. Cadmium, an element that is not essential for the human body, has the potential to induce diseases such as “Itai-Itai” as a result of the excessive buildup of cadmium ions in water[7]. Arsenic is present in water in the forms of arsenite [As (III)] and arsenate [As (V)]. It has been observed that As (III) is significantly more toxic than As (V), with toxicity levels ranging from 20 to 60 times higher. This is attributed to the fact that As (III) represents a stable form of arsenic compounds[8,9]. Lead, like other heavy metals, is commonly employed in various industrial applications, including but not limited to batteries, pigments, and alloys. The consumption of water that is highly contaminated with lead can result in neurotoxic effects on the human body, especially in children[10]. Therefore, it is imperative that these metallic ions of high atomic weight be accurately quantified. Subsequently, the significant reduction in their effectiveness is an additional primary concern.

4. Sensing of heavy metal ions

As previously discussed, it is unnecessary to reiterate that PEG exhibits distinctive properties that make it a widely utilised material in various research applications such as sensing, removal of heavy metal ions, in cosmetics, plant industry, pharmaceutical, textile industries, etc. PEG has gained increasing attention as a desirable functionalizing agent for the detection of heavy metal ions, which are a significant component of water pollution in aquatic environments. Indeed, PEG exhibits a strong attraction towards hydroxyl and amino functional groups (see **Figure 4**). Both groups possess a distinctive binding capability with a range of biomolecules, enabling them to effectively detect and analyse analytes. Consequently, these materials are adorned with noble metal nanoparticles, metal-oxides. Several activation techniques can be employed to modify the lone hydroxyl group in the methoxy form or the two hydroxyl groups in PEG diol, rendering them reactive towards various chemical groups. Currently, there exists a variety of commercially accessible activated polyethylene glycols (PEGs). The derivatives under consideration are frequently monofunctional, exhibiting either a linear or branching configuration. **Figure 5** displays the chemical structures of some significant PEG derivatives. These derivatives are mostly recognised by their molecular weight (Mw)[13,14].

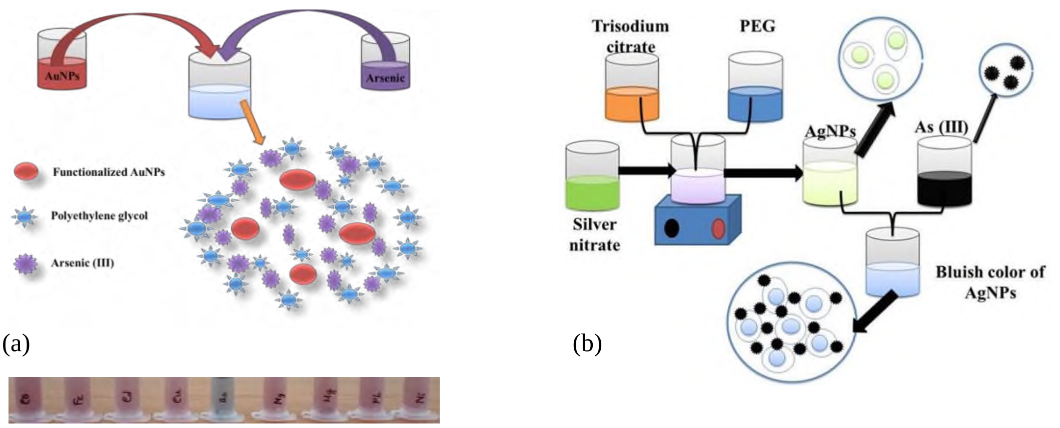

Figure 4. Assessment of heavy metal ions **(a)** PEG Functionalized AuNPs (modified after the study of Baruah and Biswas[26]); and **(b)** PEG Functionalized AgNPs (reproduced from the study of Bai et al.[25] with permission).

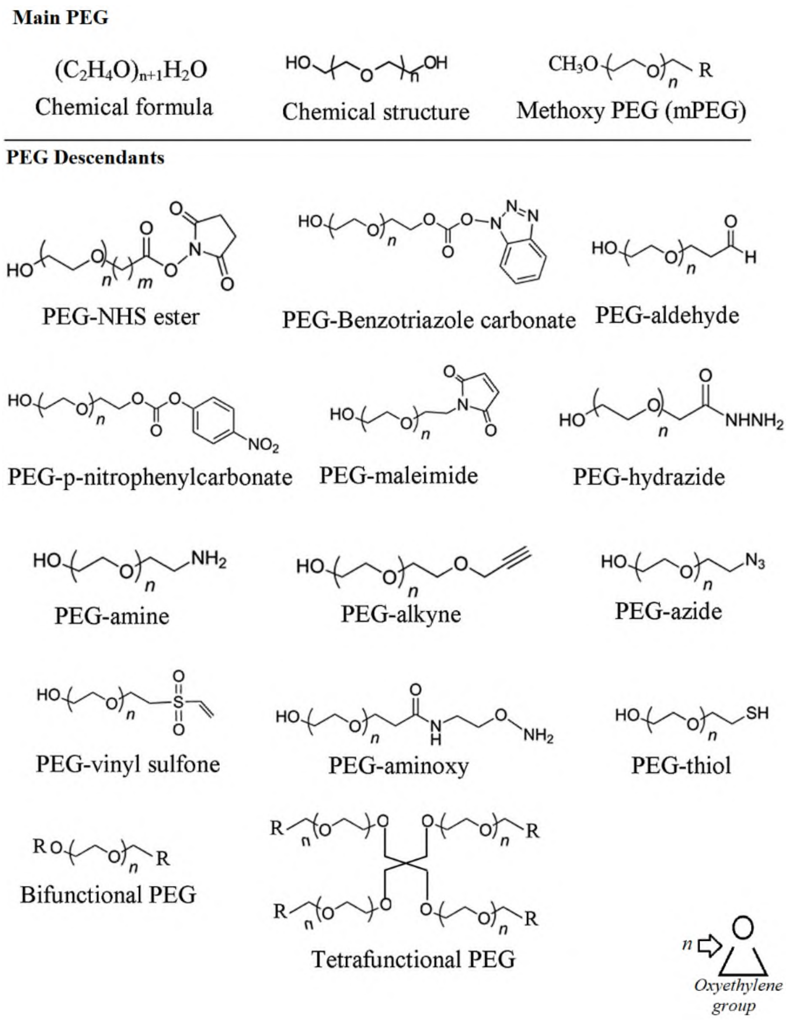

Figure 5. PEG and its' derivatives (modified after the study of D'souza and Shegokar[14]).

Under such conditions, the probes become impregnated with PEG decorated composites near the heavy metal ions. The PEG present in these composites specifically functions as a receptor for the metal ions. As a result, modulation in either intensity or frequency/wavelength occurs, depending on the specific type of interrogation. In the context of electrochemical sensing, the measurement is obtained by observing alterations in capacitance, resistance, or current/voltage. **Table 1** enlists the works on heavy metal ion sensing through PEG functionalization.

As evident in these works, the selectivity and specificity were attributed to PEG. Starting from nanoparticle functionalization such as gold, silver, copper, etc. to graphene quantum dots, assessment of heavy metal ions has been performed exclusively. Many of these reported works attained limit of detection up to 1–2 ppb level[18,19,25,26] which remained within the permissible limit of WHO. Apart from this, PEG functionalized special electrodes with graphene/ITO (Indium Tin Oxide) embedment showed superior muti-ion detection as compared to colorimetric. Meanwhile, spectro-fluorescence based identification also performed well as evident in the table.

Table 1. Sensing of different heavy metal ions via PEG Functionalization.

Detection protocol	Functionalization and detection matrix	Heavy metal ion	Reference
Spectro fluorescence	PEG-PS resin beads	Cu (II) & Zn (II)	[20]
Spectro fluorescence	PEG macromonomer-based fluorescent hydrogel	Cu^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+} and Ni^{2+}	[21]
Fluorescence	PEG-based Carbon Dots	Cr^{6+}, Cu^{2+} and Fe^{3+}	[22]
Fluorescence	Schiff base derivative with carboxylated polyethylene glycol	Al^{3+}	[23]
Colorimetric	PEG Functionalization over AgNPs	As^{+}	[24]
Intensity Modulation	PEG Functionalization over AuNPs	As^{+}	[25]
Electrochemical	PEG-SH/SePs/AuNPs modified carbon paper electrode	Hg^{+}	[26]
Electrochemical	PEG GQDs	Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, and Mn^{2+}	[27]
Colorimetric	GNR-PEG-DMSA	As^{3+} and As^{5+}	[28]
Electrochemical	PEG-Pb-GQDs	Fe^{3+}, Cu^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Pb^{2+} and Mn^{2}	[29]

5. Future perspectives

Plasmas have the capability to generate polymer thin films that preserve certain chemical characteristics inherent to the monomer. The monomer fragments that have undergone radicalization exhibit an affinity for the substrate surface, as well as for each other, resulting in the formation of a widely distributed surface coating commonly known as a plasma polymer. The current technology employed for polymer synthesis enables the production of adherent and uninterrupted coatings on a diverse array of substrates, such as polyethylene glycol (PEG). This diverse range of monomers offers a wide range of chemical functionalities for subsequent enhanced immobilization characteristics of biomolecules on substrates intended for utilization in microarray and sensory assay applications[30–33]. Likewise, Internet of Things as well as machine learning will directly enhance the evaluating capacity of sensory assays deployed for heavy metal ion sensing when complex matrices are incorporated.

6. Final remark and way forward

In conclusion, this mini review has examined the remarkable polymer PEG, with a specific focus on sensing of heavy metal ions. In this context, a succinct overview is provided regarding the detection of heavy metal ions using PEG. The salient points can be summarized as follows.

- The sensing strategy has been concisely depicted as well. It is evident that a substantial body of research exists pertaining to the determination of trace amounts of heavy metal ions. Nevertheless, there are two specific aspects that require careful consideration.
- The analysis of actual samples is still in its early stages of development. A significant portion of the documented research is limited to controlled experimental settings.
- The current imperative is to strategize the implementation of on-site analysis for heavy metal ions using PEG conjugates.
- An additional aspect to consider is the efficient management of the hazardous residue that persists following experimental procedures.

While PEG exhibits inherent biodegradability, it is worth noting that the conjugating agents commonly employed in its synthesis may not possess environmentally friendly properties. Therefore, it is recommended to employ biofriendly conjugates in conjunction with PEG to effectively eliminate the residues resulting from the detection procedures. It is believed that the emerging technologies such as point-of-care, on-site sensing etc., with succinct control of conjugation of PEG over interrogating substrate can lead to ultrafast sensing of these pervasive metal ions. Inclusion of Internet of Things as well as machine learning will give extra boon to these sensing technologies.

Conflict of interest

The author declares no conflict of interest.

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