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Reasons for High Adsorption Efficiencies in Lead Removal from Aquatic Solution †

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Abstract: Heavy metals are of great concern worldwide in terms of environmental pollution due to their effects, such as persistence in the environment, bioaccumulation, and toxicity for organisms. These pollutants in a non-biodegradable inorganic form are released into water, soil, and air from different industrial sectors Lead ions are also a toxic heavy metal in terms of human health and this pollutant is permanent in the ecosystem. Among the many treatment methods, adsorption is an inexpensive, eco-friendly, and efficient process for removing Pb ions from water contaminated with lead ions. The most important detail that draws attention both in our research of the literature and in our own studies is that very high removal efficiencies of lead ions can be obtained with many different inorganic and organic adsorbents. Such high removal efficiencies cannot be obtained for other heavy metals and metalloids. Therefore, this study aimed to reveal the difference in the adsorption process of lead. The physicochemical and biological properties of lead ions and the effects of specific properties, such as amphoteric structure, free electron, post-transition metal, and the low melting temperature, were investigated accordingly.

Keywords: adsorption; amphoteric structure; high removal yield; lead ion

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1. Introduction

Although the restriction of anthropogenic activities during the COVID-19 pandemic process minimized the pressure on environmental pollution, the rapid normalization and growth process in the fields of energy, agriculture, and industry rapidly increased environmental pollution. Pollutants that cause environmental pollution are toxic and permanent. Generally, heavy metals take the first place in the environmental toxic substances class and cause significant damage by affecting the entire ecosystem [1,2]. These damages are due to their non-biodegradability, high toxicity, and large discharges into the environment [3,4].

Lead has a toxic effect for all living groups due to its properties, such as entering the food chain, being absorbed, and accumulating in the tissues [5]. It is a non-biodegradable metal that can cause diseases such as cancer, anemia, kidney failure, and neurological effects in humans [6–9]. In particular, Pb emissions are high as a result of industry-based anthropogenic activities (automobile industry, tetra-ethyl production, battery production, cable production, the ceramics industry, gasoline) [10]. Pb is a pollutant with a high molecular weight and the greatest global spread compared to other heavy metals, and it is an important factor in water pollution. In this direction, Pb removal from different water environments is one of the priority tasks of all countries in the world [11,12]. The most important reason for this priority is that Pb is one of the most stable and toxic ions in various aquatic ecosystems. Table 1 shows some specific features, sources, and permissible limit values of Pb on an international scale [13–15].

Table 1. Specific properties, sources, and international limits of Pb [13–15].

Permissible Limits			
WHO	**USEPA**	**EPA**	
0.01 mg/L	0.01 mg/L	0.015 mg/L	
Properties			
Density	Atomic Weight	Heat of fusion	Heat Capacity
11.34 g/cm$_3$	207.2 g/mol	4.77 kJ/mol	0.13 J/g K
Electron affinity	Boiling point		Melting Point
35.1 kJ/mol	1740 °C		327.5 °C
Sources			
Metal plating, Paint, Laundry process, Mining sector, Battery manufacturing, Steel industries, Alloys, Ceramics, Plastics, Glassware			

For years, a wide variety of treatment methods have been applied to remove heavy metals from receiving environments; for example, electrochemical processes [16], chemical precipitation and coagulation [17], filtration method (membrane systems) [18,19], ion exchange [20,21], and adsorption [22,23]. Due to the disadvantages such as yield variability, high cost, large area requirement in these treatment processes, adsorption, which is a physico-chemical increase method, comes to the fore with advantages such as easy applicability, low cost, and adsorbent regeneration [24]. Many types of adsorbent/biosorbent (microbial biomass, seaweeds, waste sludge, agricultural wastes, natural wastes, natural minerals, water-based wastes) have been applied to remove Pb from aqueous solutions [25].

The most important detail that draws attention both in the research in the literature and in our own studies is that very high removal efficiencies of lead ions can be obtained with many different inorganic and organic adsorbents. Such high removal efficiencies cannot be obtained for other heavy metals and metalloids. Therefore, in this study, it was aimed to reveal the physico-chemical and biological properties of lead ion and the effects of specific properties such as amphoteric structure, free electron, post-transition metal, and low melting temperature on the adsorption process of lead in order to reveal the difference in the adsorption process of lead.

2. Materials and Methods

"*Web of Science Core Collection; Science Direct*, *Springer*, *Wiley*, *Taylor & Francois*, *Scopus*" *(Clarivate Analytics*®, *Boston*, *USA) and* "*Google Scholar*" *(Googleplex*, *Mountain View*, *California*, *United States)* were the databases used in this study. Bibliometric analysis was performed based on these databases.

First, a general search was performed using the keywords "*lead adsorption/biosorption*", "*adsorbent/biosorbent effect*", *and* "*high ad-sorption efficiencies*" in the basic search tool. For this research, the search has been narrowed down to specific terms. In this context, the keywords "*free electron*", "*amfoter structure*", "*Liquid Metal*", "*low melting temperature*", "*weak metal*", "*post-transition metal*" were researched to cover the last 4 years. Forty articles were evaluated according to the field of interest of this research. In addition, the applications, including the adsorption processes related to Pb purification, which were undertaken before in the study, were carried out according to international experimental procedures [26–28].

3. Results

The most important detail that draws attention both in the research in the literature and in our own studies is that very high removal efficiencies of lead ions can be obtained with many different inorganic and organic adsorbents. This situation is associated with some properties and factors specific to Pb.

3.1. Low Melting Liquid Metal State

Low melting point metals and post-transition metal alloys are materials with admirable properties that are described as "liquid metals" in the literature. Some specific properties of liquid metals (fluidity, flexibility, conductivity, alloying potential) are properties that do not coexist in other metals and materials. Due to these interesting properties, these metals are used in many sectors [29,30]. Mercury (Hg), gallium (Ga), rubidium (Rb), cesium (Cs), and francium (Fr) are included in this group because liquid metals are typically in liquid form at $\leq$23 $\pm$ 2 °C (room temperature) levels [31]. In order to increase the access and application of liquid metals, which are limited in terms of both need and use today, the room temperature definition was increased to 330 °C and post-transition metals (indium, thallium, tin, lead (Pb), and bismuth) were added to this group (Figure 1) [32,33].

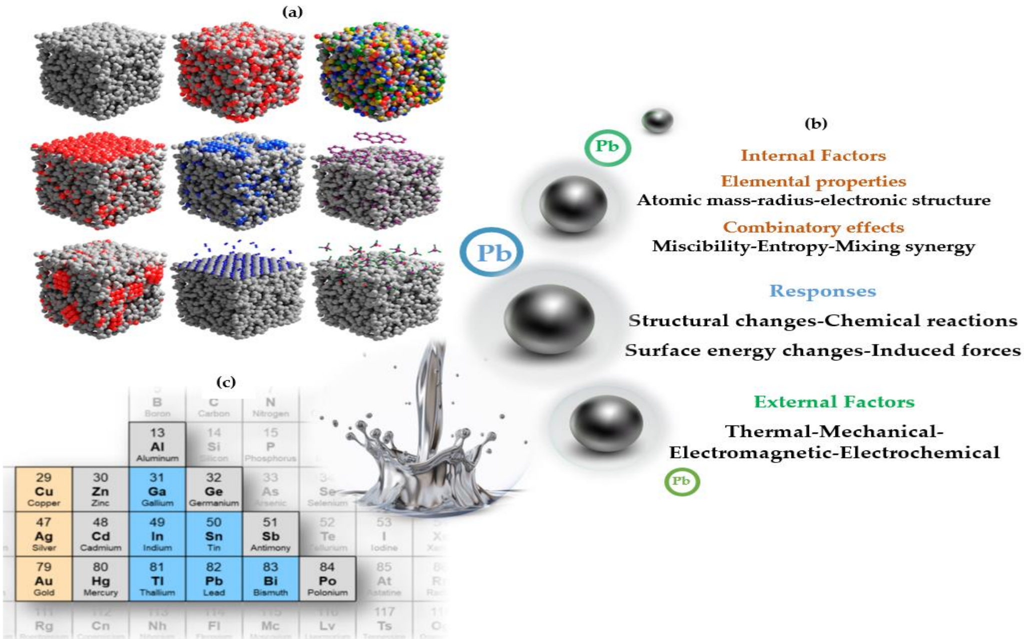

Figure 1. (**a**) Bubble dispersions of liquid metals (such as surface layering, alloy formation) (**b**) Liquid metal potential: internal and external factors and possible reactions; (**c**) Post-transition metals (blue) in the periodic table and those considered as post-transition metals (gray and light orange) (adapted from [32]).

In terms of current needs and heavy metal pollution removal, post-transition metals (especially Pb) have different electron arrangement for metallic bonding than other metal species. This increases the polarizing ability and promotes the tendency to form covalent bonds. Electron state and liquid nature provide the ability for Pb to exhibit both metallic and non-metallic properties (surface stratification). Some non-simple properties of Pb and liquid metals are shown in Figure 1.

3.2. Post-Transition Metal and Electron Distribution

Post-transition metals are also called weak metals in the literature. Post-transition group metals are in the p block of the periodic table, and Pb is also in this group. This group, including Pb, is between metalloids and transition metals. At this point, they are denser than transition metals and less densely electro-positive than other metals (alkali and alkaline earth groups) [34,35]. The weak metals class includes aluminum, gallium, indium, tin, thallium, lead, and bismuth (see Figure 1c). As seen in Table 1, Pb is a blue-silver mixed post-transition metal with an atomic number of 82, an atomic mass of 207.19, and has four stable isotopes. Although the structure of Pb is surrounded by four open electrons, it usually takes +2 valence instead of +4 in different structures. The other two electrons can simply be ionized. The two-electron effect can be an effect factor in the adsorption process and other applications.

3.3. Amphoter/Amphoteric Structure

In the fields of Environment and Chemistry, amphoteric/amphoteric structure means that it can react with both acid and base. It means "*Ampho: both*", and an amphoteric metal has a reversible effect like a base in an acid medium and an acid in a basic medium [36,37]. The Brønsted–Lowry acid–base theory also confirms this. In other words, they are amphiprotic molecules that can donate or accept a proton (H^+). Amphoteric oxides consist of metal groups. Many metals (such as zinc, tin, lead, aluminum, and beryllium) have the potential to form amphoteric oxides or hydroxides. In terms of Pb, the amphoteric effect may play a key role in the adsorption/biosorption processes according to the adsorbent structure.

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O \quad (1)$$

$$PbO + 2NaOH + H_2O \rightarrow Na_2[Pb(OH)_4] \quad (2)$$

3.4. Adsorption/Biosorption Pre-Treatment Studies

Among the many treatment methods, adsorption is an inexpensive, environmentally friendly, and efficient process for removing Pb ions from water contaminated with lead ions. The most important detail that draws attention both in the research in the literature and in the laboratory-scale pretreatment studies we have performed is that very high removal efficiencies of Pb ions can be obtained with many different inorganic/organic adsorbents and biosorbents (see Figure 2). In this case, as we mentioned in the conclusion section, it is due to some specific properties and the adsorbent/biosorbent structures (surface analysis, pore distributions) used [15,38–40].

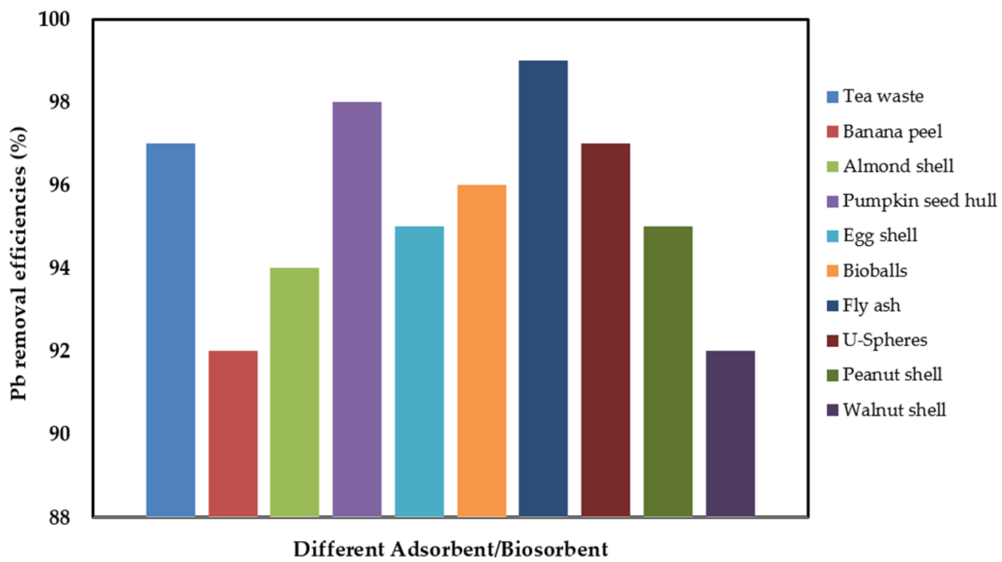

Figure 2. Pre-treatment values for Pb made with different adsorbents/biosorbents.

4. Discussion

Adsorption and biosorption processes are methods that allow for the use of different sorbents, and they are especially used in the purification of heavy metals from the aquatic ecosystem. Pb is also successfully removed from receiving water environments by these methods. The interesting point is that the removal of Pb with each sorbent is high compared to other metals. It can be said that this depends on some specific factors or situations. We can list them as follows:

1. Active components (pectin, catechin, lignin, etc.) in the structures of adsorbents and biosorbents and functional groups (carboxyl:-O, amines: -NH, and hydroxyl: -OH) of these sorbents can show a strong interaction with Pb.
2. The amphoteric/amphoteric nature of Pb may increase the removal rate.
3. Another factor is that some of the physical properties of Pb (high density, molecular weight, etc.) are different from those of other metals.
4. Being in the liquid metal group free two electron distribution can affect the adhesion to the surface of the sorbents in the adsorption mechanism.
5. The nature of the sorbents, their amphoteric properties, and the modification stages explain the bonding and sorption mechanisms of Pb.

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