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A theoretical overview of heavy metal treatment with agricultural wastes

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Abstract

Tomato plant between Pb$^{2+}$, Cd$^{2+}$ with tomato waste having amino and the other functional groups waste contain cellulose materials (lignin), polysaccharides having functional groups having the ability of binding heavy metals as sorbents is commonly cultivated plant for its fruits. Aim of this study to determine the best alternative way to search the binding capacity of agricultural waste as theoretical to remove heavy metals with tomato plant from waste waters as economically by comparing experimental results respectively. The capacities of adsorption for heavy metals (Pb(II), Cu(II) and Cd(II)) of the tomato plant residue were 0.092, 0.533 and 0.238 mmol/g sorbent. As theoretical, HF (Hartree-fock), lanl2dz methods were used for molecular calculation. The theoretical calculations were carried out by means of the lanl2dz functional base. The chemical activities were calculated by using this method. The removal of Pb$^{2+}$ and Cd$^{2+}$ found lower than Cu$^{2+}$ because of the strong complex formation as experimental and theoretical calculations supported this issue. Theoretical calculations are important to prevent loss of time and cost.

Keywords: Pb(II), Cu(II), Cd(II), biomass, HF, docking, heavy metals

1. INTRODUCTION

Solid waste management is an important system because of involving multiple subsystems inputs, materials and resources to process waste properly [1]. The role of ecosystems in decreasing the effects of common agricultural wastes is recognized in several trimmer measures and public policy attempts in many parts of the world [2]. Heavy metals are hazardous substances to the human body, animals and plants because they accumulate in the cells of them. They are used a lot of industrial activities for example, battery manufacturing, electroplating, mine-processing, production of paint and fertilizer materials, etc. When the acid rain reaches the soil, some heavy metals go into ground water, lakes and rivers. Moreover the heavy metals of industrial wastes with soil and then the water reaches to the living organisms and they are taken into the human body with the consumption products from soil and drinking water [3-7].

Some of the heavy metals is lead, copper and cadmium. Lead is one of the hazardous heavy metal to the living organisms. If it gets into human body, it causes harmful effects. For example; it can damage red blood cells and decrease the ability of carrying oxygen to the tissues. It is also harmful for nerves system and kidneys. Especially, young children and babies are at the risk of lead poisoning. Lead is the main inhibitor of some enzymes as well [8,9].

The other hazardous heavy metal for living organisms is Cadmium. The mainly used industrial areas are cadmium-nickel batteries, mining alloys, pigment and fertilizers. The harmful effects of the human body are acute and chronic metabolic disorders such as renal damage, hypertension and emphysema [8]. Copper is commonly used heavy metal in industrial areas such as electrical products and also highly found as industrial wastes. Intaking of the required quantitative is essential
but excessive of have toxicity to the human body such as itching, dimerization and soles of feat [10,11].

The notification of effecting heavy metal ions to the living organisms, the water quality is the important to focus on. Many methods, chemical and physical, of have been used for the elimination of heavy metals from polluted waters with the industrial wastes. Chemical precipitation, filtration, ion-exchange, electrochemical treatments, coagulation, evaporation, membrane separation are some of them [12-16]. These methods have some disadvantages. For example, the chemical precipitation; chemical substances are costly and poor recovery heavy metals [17,18]. The most applicable alternative method is biosorption because it has high efficiency and economically to purify waste water [19-22].

In recent years, natural harvested agricultural biomaterials have been used to remove heavy metals from polluted waters as sorbent due to low operating cost, relative abundance, specific selectivity of metal interest and not having the other compounds. Some of the biosorbents is rice husk [23],tobacco steam, pine bark [24], moringa oleifera [25], saw dust [26], cashew nut shell [27], cork biomass [28], barley straw [29], lignin [30], loquat bark [31] and tomato waste [32]. The new method should be cheap and save up time.

In the functional groups of tomato residues are determined with using FTIR (Fourier transform infrared spectroscopy) by Goatha et al. And also the functionals groups of tomato plant waste, metal binding are shown in Fig 1 [32] by them. The using of tomato plant residues is preferred due to not having commercials values, simple preparation and the local availability [32].

Tomato has been cultivated commonly for its fruits. After harvesting, the residues of tomato plant are generally burned and not having commercial value. They contain cellulose materials (lignin), polysaccharides that have functional groups having the ability of binding heavy metals as sorbents [33,34]. Because of having many functional groups and strong metal affinity, they are preferred to instead of the expensive synthetic biosorbents [35-37]. In this study; the best alternative way will be determined to search the binding capacity of agricultural waste as theoretical to remove heavy metals with tomato plant from waste waters as economically by comparing experimental results respectively. Make justified all lines as we do in this style guide.

2. EXPERIMENTAL

2.1. Materials and method

In this study; Pb(II), Cu(II), Cd(II) were used as the heavy metal ions. The metal ion solutions were firstly taken 1000 mg/L after that they were prepared for atomic absorption standard stock metal solution as the water down to the necessary concentrations (100 mg/L).

The dried tomato plant residues were collected waste forms from the field of Laçin, the village of Eskişehir in Turkey, washed three times with distilled water, dried at 60-80 °C overnight and turned into particles, as a sorbent. After putting them into plastic bottles, 0.05 g the dilutions were made for the required concentrations (100 mg/L).

The sample was shaken at 125 rpm at 25 °C for about 2 h. The content mixture was centrifuged for 10 min. The concentrations of Pb(II), Cu(II), Cd(II) in mixture were analyzed by using AAS (Atomic absorption spectroscopy). The amount of biosorbed metal ions to per grams of biomass was calculated this equitation:

\[ q = \frac{(C_i - C_{eq}) V}{m} \]  

\[ q \quad (\text{mg/g}) \]
\[ C_i \ (\text{Initial concentration (mg/L)}) \]
\[ C_{eq} \ (\text{Equilibrium concentration (mg/L)}) \]
\[ V \ (\text{Volume of the medium (L)}) \]
\[ m \ (\text{Amount of biomass (g)}) \]
3. THEORETICAL

3.1. Materials and Method

The electronic structures of tomato-heavy metals complex are observed by HF, lanl2dz methods and it was used for geometry optimization. The theoretical calculations were performed by means of the lanl2dz functional. The theoretical values were obtained by using the result of HF method [39,40]. The structure activity of the compounds using this method were indicated and appraised.

4. RESULTS AND DISCUSSION

4.1. Experimental

The biosorption capacities of the tomato plant waste for the selected heavy metals Pb(II), Cu(II) and Cd(II) were 0.092, 0.533 and 0.238 mmol/g sorbent, respectively, in dried tomato biomass waste at pH=7 (approximately) and at 25 °C. The adsorption competitions of all the heavy metal ions were the evident of degree of the metal uptakes in dried tomato biomass waste. Initially, the heavy metal concentrations, the metal sorption capacity of Cu(II) among three heavy metals was the highest in tomato plant biomass waste. On the other hand, the metal loadings order were Cu(II)> Cd(II)> Pb(II) from high to low.

The differences capacity of adsorption for the selected metals is possibly related to the electronegativities of the cations [46]. To comprehend of the binding sites on the biomass (tomato waste) surface, a thermodynamic model (HF includes lanl2dz base) could be improved by explaining of the capacity of the active metal ion adsorption sites on the surfaces of the tomato plant waste to indicate the binding ability of heavy metal ions on the surface of the biomass such as adsorption and coagulation.

As a not common commercial agricultural and natural cellulosic biomass, tomato plant waste is a complex materials having cellulose materials (lignin), hemicellulose and polysaccharides as the mainly compounds. These compounds ordinarily have more polar functional groups, as amines, alcohols, carboxylic acids and phenolic hydroxides. The polar functional groups mentioned above may participate to get the existing of the charged sites on the surfaces of biomass [32,41]. It may be partly taking into account for the capability of the biomass to catch cations in stability compose by forces such as, coulombic, electrostatic forces and covalent bonding forces of some these cations. The biomass surface charge also plays an important role in electrostatic adsorption on the biomass of tomato. Shortage of fresh water is serious problem for many regions. A lot of various desalination technologies is used to solve this problem [42]. One of them is biosorption.

4.2. Theoretical

The Gibbs Free Energy of Tomato+Cu$^{2+}$, Tomato+Pb$^{2+}$ and Tomato+Cd$^{2+}$ are given in Table 1 (The values are given as Hartree; 1 Hartree=627.5095 kcal. mol$^{-1}$).

|            | HF(lanl2dz) Separately | DFT (Together) | ΔG(Hartree) | ΔG(Difference Hartree) |
|------------|------------------------|----------------|-------------|------------------------|
| Tomato+Cu$^{2+}$ | -1064.22072            | Tomato-Cu$^{2+}$ | -1458.42860 | -394.20788             |
| Tomato+Pb$^{2+}$ | -873.16663             | Tomato-Pb$^{2+}$  | -885.46740  | -12.30084              |
| Tomato+Cd$^{2+}$ | -916.01128             | Tomato-Cd$^{2+}$  | -1012.93612 | -96.92484              |
| Tomato      | -869.22643             |                 |             |                       |

The values of Gibss free energy (difference) from Table 1 are -394.20788, -96.92484 and -12.30084 Hartree. The order from high to low is Tomato-Cu$^{2+}$>Tomato-Cd$^{2+}$> Tomato-Pb$^{2+}$. The experimental sorbent capacity is the same order with these theoretical values. Cheng et al. emphasized that the negative value of ΔG° of Pb(II) ion and the decreasing value of ΔG° proved that the adsorption process was spontaneous and more favorable [43]. In our study; The theoretical calculations are supported with the experimental results of Cheng et al [43].

HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), Δ(HOMO-LUMO) and dipole moments of Tomato+Cu$^{2+}$, Tomato+Pb$^{2+}$ and Tomato+Cd$^{2+}$ are given in the Table 2.
The removal of Pb\(^{2+}\) and Cd\(^{2+}\) with tomato waste and docking results are also supported this issue as seen in Table 3.

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| Docking Results | E total |
|-----------------|---------|
| Tomato-Cd       | -39.01  |
| Cd\(^{2+}\)-tomato-Cd | -43.83  |
| Tomato-Cu       | -38.34  |
| Cu\(^{2+}\)-tomato-Cu | -30.63  |
| CuSO\(_4\)-tomato-Cu | -29.25  |
| Tomato-Pb       | -38.34  |
| Pb\(^{2+}\)-tomato-Pb | -43.85  |
| Pb(NO\(_3\))\(_2\)-tomato-Pb | -46.89  |

The removal of Pb\(^{2+}\) and Cd\(^{2+}\) found lower than Cu\(^{2+}\) because of the strong complex formation between Pb\(^{2+}\), Cd\(^{2+}\) with tomato waste and docking results are also supported this issue as seen in Table 3.

Setyono and Valiyaveettil indicated that the desorption efficiencies of heavy metal ions, especially Ni\(^{2+}\), Cd\(^{2+}\), and Cr(VI) were lower than Cu\(^{2+}\) due to strong complexation with amine groups of functionalized paper [44]. The thermodynamics values of Pb(II) adsorption onto the tobacco stems shown that the adsorption was spontaneous and endothermic [45]. In this study; the quantity of removal Cd\(^{2+}\) was also lower than Cu\(^{2+}\) as the experimental and theoretical calculations supported this issue. So, we can assume that the removal of Pb\(^{2+}\) and Cd\(^{2+}\) is lower than Cu\(^{2+}\) because of the strong complex formation between Pb\(^{2+}\), Cd\(^{2+}\) with tomato waste due to having amino and the other functional groups.

5. CONCLUSIONS

In this experimental and theoretical study, the heavy metals binding efficiency of tomato plant waste was investigated and the indicated result can be reached; The tomato plant waste exhibited a strong binding capacity for the heavy metals as being calculated in this study; Pb(II), Cu(II) and Cd(II), with respective equilibrium loadings of 19.06, 33.87 and 26.76 mg of metal per g of biosorbent. Theoretical calculations are applied the other heavy metals and agricultural wastes due to be supported experimental results as mentioned above.

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