Production of Biosorbents from Agricultural by-product and theirs Adsorption Characteristics for Metal ions

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Abstract

The project concerns to adsorptive elimination of heavy metal ions from aqueous solution, namely to synthesis, modifying, studying of properties and to application combined biosorbents on the base of materials from agricultural by products. The main purpose is preparation of effective biosorbents for elimination of heavy metals ions from aqueous systems.

The potential to remove metal ions from aqueous solutions through biosorption using the straws and shells of agricultural by products (such as barley, hazelnut etc.) was investigated. The batch experiments will be completed previous studies will be discussed. The effects of the significant process parameters such as initial pH, change in pH during adsorption, contact time, adsorbent amount, and the initial metal ion concentration will interpreted from the data realized from batch studies.

These low-cost adsorbents developed from the naturally and abundantly available are biodegradable. The advantages of these materials include availability, low-cost, and a reasonable metal sorption capacity. Within their complex structure, agro-waste materials have functional groups that play a major role in metal ion sorption. Agro-waste materials functional groups are associated, in part, to carboxyl, hydroxyl groups and phenolic: these oxygen-containing sites play an important role in the metal ion removal. The most probable metal sorption mechanisms are ion exchange and complexation and partly physical adsorption and electrostatic attraction.

Keywords: Biosorption, heavy metal, low cost adsorbents, isotherms, pollution

Research Proposal:

Project Title: Production of Biosorbents from Agricultural by-product and theirs Adsorption Characteristics for Metal ions

Project Information

State of the art: The project concerns to adsorptive elimination of heavy metal ions from wastewater, namely to synthesis, modifying, studying of properties and to application combined adsorbents on the base of materials from agricultural waste products.

Biosorption capacity depends not only on the porous structure of the sorbent but also on its chemical structure. In order to characterize the adsorption capacity of a material, determining its surface area and pore size distribution would not be enough, it being often those carbons having the same surface area exhibit different sorptive behavior. This has led some researcher to propose alternative models for the sorption capacity evaluation, standing out those based on sorption from aqueous solutions of cationic and anionic biosorbents.

Sewage, contaminated by heavy metals, arises during use of water in very wide spectrum of industrial productions. Thus the metals getting in water can be in the various forms and, accordingly, demand various methods of processing.

Problem statement:

Among chemical substances, which pollute an environment, the heavy metals and their substances present a considerable group of toxicants are capable to cause harmful influence on a human health. Danger of heavy metals is caused by stability of their ions in exterior medium, solubility in water, sorption by a soil and migration ability on a chain “soil - plant - animal - man”, and it makes to accumulation in dangerous concentrations in the living organism and occurrence of a lot of ecology dependent diseases.

Taking into account the general pollution of an environment by heavy metals ions and the threat caused by it to health of people and animals, the requirement for manufacture of new effective biosorbents, food and fodder additives of protective, antidote and neutralize action has got actuality and the social importance. Economic feasibility of carrying out of researches in this area is grounded, firstly, on possibility to use cheap mostly non-utilized waste products of agriculture, food and a process industry, and, secondly, on creation of manufacturing wide

assortment new sorption materials of selective action. This research is devoted to development of ways of updating of agricultural by products with the purpose of improvement of their ability to selective removal of ions of heavy metals.

Objective: The main tasks of the project are:

The objectives of this study are

1) to develop the adsorbents from agricultural wastes for sorption/recovery heavy metals from aquatic medium.
2) to characterize in detail untreated and chemically modified agricultural by products using elemental and porosity analysis, Fourier transform infrared spectroscopy (FTIR).
3) to examine the sorption/desorption behaviors of metal ions with untreated and chemically modified agricultural by products.
4) to examine the effect of initial metal concentration, pH, and temperature, amount of adsorbent and time on the equilibrium.
5) Investigation of physico-chemical properties of all combined biosorbent components-sorptive pore volume, specific surface area, ion-exchange capacity, different isotherms.
6) Application of self-prepared biosorbents for pollutants removal from water and wastewater inclusive residue analytical determination of their efficiency.

1. Introduction

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The problem of removing pollutants from water and wastewater has grown with rapid industrialization. The discharge of toxic metals into watercourses is a serious pollution problem, which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect. The removal of metal ions from effluents is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods. Less well-developed countries are expanding their industries, often with serious accompanying pollution. Recently, increased interest in the application of various biosorbents in metal ions removal and recovery has been observed. Agricultural by products are abundant in the nature. Such systems related to using sorbents may be based on biomasses derived from waste products from wood industries or low-cost material harvested. It is recommended that the adsorbent is available in large quantities and very low-cost. Most available technologies applied in the removal of metal contaminants in aqueous systems use the well established processes of adsorption. Biosorbents currently in use are either too expensive or not readily available for wastewater treatment.

In general, a biosorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Biosorption is a promising technique for the removal of heavy metals from aqueous environments especially when adsorbents are derived from lignocelluloses materials.

The main sources of metal ions in aquatic life are discharged waste streams from chemicals, pulp and paper manufacturing processes, metal plating, mining operations, refining ores, paint and pigments, tanneries, sludge disposal, radiator manufacturing, smelting, alloy industries and storage batteries industries, steel works with galvanizing lines, brass metal works, brass plating, viscose rayon yarn and fiber production, etc.

Various treatment technologies have been developed for the decontamination of water and wastewater contaminated with heavy metals. The most commonly used methods for the removal

of metal ions from industrial effluents include: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electro dialysis, electrolytic extraction, reverse osmosis, ion-exchange, evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, stem stripping, flocculation, sedimentation, soil flushing/washing chelation, etc. Most of these methods suffer from drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries.

There is a need to develop new adsorbents which are readily available at low cost to remove metal contaminants in aqueous system. Low cost forest and agricultural wastes without or with little processing are considered promising adsorbents for heavy metals due to their high surface areas, micro porous characters and surface chemical natures. Conversion of this waste to a useful adsorbent contributes not only for the treatment of heavy metals contaminated environment but also to minimizing the solid wastes.

In this work, nutshells, hazelnut shells, almond shells, barley straw, wheat straw and different other agricultural waste materials will be utilized as the raw material for the production of biosorbents by chemical treatment and their adsorption capacity for metal ion will be evaluated. In order to increase the adsorption capacities and decrease the leaching of extractive matters from all investigated biomasses, they will be modified with some organic materials such as citric acid, oxalic acid, tartaric acid etc. The potential to remove metal ions from aqueous solutions through sorption using these modified and unmodified sorbents will investigated by trying them in batch experiments. The effect of the most significant process parameters (pH, adsorbent dosage, equilibrium time, initial concentration of metal ions on biosorption equilibrium was studied.

2. Materials and Experimental Work

2.1. Materials

The raw materials used in this work as biosorbents will be the agricultural wastes which will be collected from Anatolia, Turkey. All the chemicals used were of analytical reagent grade. All the solutions were prepared with double-distilled water.

2.2. Apparatus

All biosorbents will be grinded with a grinding machine. The pH measurements will be performed with a pH meter. A thermo stated shaker and a magnetic stirrer will be used for sorption experiments. The analysis of metal ions will be carried out colorimetrically with the 1,5 diphenyl carbazide method by using a UV-Visible Spectrophotometer (Shimadzu UV-1700) (λ:540 nm) and a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS).

Elemental analysis of adsorbent will be carried out using an elemental analyzer. The elemental composition of biosorbents will be determined regarding carbon, hydrogen, nitrogen, and oxygen.

The functional groups present in the adsorbent will be characterized using the KBr translucent disk to prepare the biosorbent samples with an IR spectrometer over the wavelength region 4000–1000 cm^{-1}.

2.3. Adsorbent characterization

2.3.1. Chemical analysis

The chemical analysis of biosorbents was measured to detect its main contents using high-performance liquid chromatography (HPLC). A high-performance liquid chromatography equipped with an injector and a fluorescence spectrophotometer will be used. Also, Qualitative and Quantitative carbohydrate analysis of biosorbents was measured using (HPLC).

The results of the chemical analysis of biosorbents are useful in giving a hint of relative proportions of the different components. The contents of cellulose, protein and minerals are important for metal capturing.

2.3.2. *Carboxyl determination*

0.25 g dry sample is taken in water and 0.1 N NaOH is added and stirred for 24 h. The mixture is back-titrated with 0.1 N HCl to the phenolphthalein end point. Conversion factors are determined using citric acid as standard. Untreated biosorbents are used for controlling purpose.

2.3.3. Infrared spectra of the okra waste

The biosorption of metal ion will be studied by Fourier transform infrared spectroscopy (FTIR), which suggested that the presence of metal ions in the biomass affects the bands

corresponding to hydroxyl and carboxyl groups. Infrared spectra (IR) of biosorbents will be obtained using a spectrophotometer. The infrared spectrum of the solid substance will be recorded on in the region 400–4000 cm^{-1}.

2.4. Modification of walnut shells with modifiers

First, citric acid (CA), tartaric acid, oxalic acid etc. is dissolved in water, added into biosorbents, thoroughly mixed and allowed to soak for 24 hours at 60°C in the oven. At this period, all surface moisture is removed and biosorbent particles are coated with modifiers. Then, the dry sample is thermo chemically reacted for 4 hours (optimum time) by elevating oven temperature at 120 °C (optimum temperature). The oven temperature and reaction time is raised to the desired level (110-130 °C) and 2 to 24 hours, respectively and mixtures are allowed to react. Reaction products are mixed in water for 30 min, filtered and washed with water. The unreacted biosorbents is determined by titration with NaOH. The product, modified biosorbents is dried in the oven. Finally, the modified shells are vacuum oven dried at 45°C for 16 h. The thermally treated sample is then cooled to room temperature and then ground.

2.5. Batch adsorption

The initial pH of the metal solution is adjusted with 0.1 mol/L HNO_3 and 0.1 mol/L NaOH respectively. To study the effect of pH on sorption, the pH of the Cr(VI) solution is adjusted to values in the pH range of 2-9. Samples (0.1 g by dry weight) are equilibrated with 20 mL, 10^{-3} M aqueous solution of metal ions at varying pH values. The biosorbents and solution is separated by filtration through a membrane filter. The filtrate is analyzed for the remaining metal ion concentration.

The concentration isotherm curves and equilibrium sorption capacities are determined in batch experiments by shaking, at prefixed times in sealed test tubes. Sorption isotherms are carried out with different initial metal concentrations varying from 0.1 to 1mM while holding the sorbent amount at 0.1 g at room temperature (25±1 °C). Contact time adsorption experiments are conducted at 25±1 °C. Time dependent experiments are carried out by shaking the adsorption mixture at various predetermined intervals (range of 5-240 min) and analyzing the metal ion content at the end of the contact time. The sorbent amount in the batch conditions is varied from

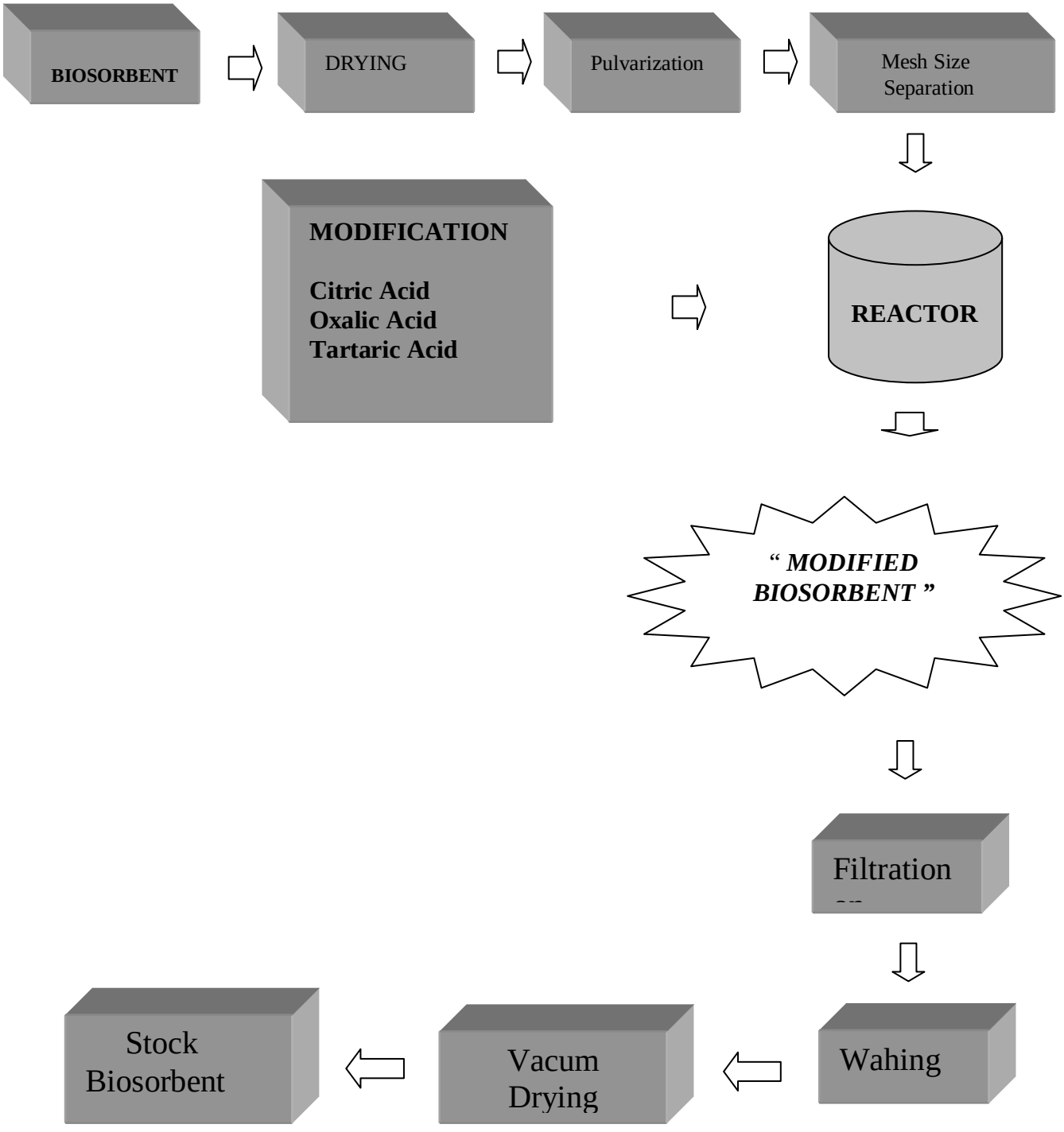
0.02 to 0.2 g for adsorption studies. The same measurements are repeated three times and average values have been taken as the remaining metal amount in the solution phase.

The Cr(VI) ion concentrations in the solutions are determined by the standard colorimetric method with 1,5-diphenylcarbazide [55]. Metal concentration in the solution was analyzed with UV–vis Spectrophotometer (λ: 540 nm) and GFAAS. The concentration of metal ions is calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption. In all cases, mass balance was confirmed. The kinetic data of adsorbed amount of metal at time t, q_t (in mg g^{-1} of adsorbent), are obtained by the mass balance.

The influence of several operating parameters, such as, particle size, different chemical treatment, contact time, pH, initial concentration and adsorbent dose was studied. The procedures for the project were given in following pages.

Flow scheme of the sorbent production

BIOSORBENT PRODUCTION



Flow scheme of the sorption system