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# Platinum recovery from model media and a Pt–Sn/alumina spent catalyst extract using corn husk-based adsorbent

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ABSTRACT

Preparation of corn husk-based adsorbent for platinum recovery is studied. The adsorbents are prepared and characterized, and the adsorption of platinum onto the adsorbents is examined. Results indicate that hydroxyl and amine groups are responsible for adsorption of platinum onto the adsorbents. Immobilized amine enhances the adsorption and aluminates interfere in adsorption of platinum ions. The adsorption capacity of the adsorbent with immobilized amine for model media and intact solution is 38.5 and 16.2 mg Pt/(g adsorbent), respectively. Structural changes of the treated corn husk is explained by Mannich mechanisms. The kinetics of adsorption of Pt follows a pseudo-second-order model.

## Introduction

Precious metals (PMs) in general and platinum group metals (PGMs) in particular are strategic metals that are rare, nonrenewable, unevenly distributed in the earth crust, usually appear with a large number of impurities in nature, and their concentrations in natural ores are usually in orders of parts per million (PPM) or parts per billion (PPB). As a result, extraction and isolation of these metals from natural resources – usually referred to as primary resources – is immeasurably cost intensive. On the other hand, currently, there are large amounts of industrial wastes such as spent catalysts from oil, gas, chemical, and petrochemical industries, spent auto catalysts, unfunctional medical devices, electric and electronic wastes, and industrial wastewaters that contain precious metals. These wastes are potentially hazardous to the environment. In addition, these wastes are many orders of magnitude more concentrated in precious metals than the primary resources [1–13]. Separation of precious metals from the so-called secondary sources of precious metals is much easier and more cost effective compared with their recovery from the primary resources. Recovery of precious metals from secondary resources would mitigate environmental concerns, and would help the preservation of natural resources through recycling.

Hydrocracking spent catalysts of petroleum industry contain high amounts of precious metals such as palladium, rhenium, and platinum. The concentration of precious metals in spent catalysts may be about five orders of magnitude higher than their concentration in raw natural resources [14].

Pyrometallurgical (dry) and hydrometallurgical (wet) methods are the common processes currently used for recovery of precious metals from secondary source of precious metals, and liquid extraction and leaching with aqua regia is the most popular method because of high efficiency and relative low cost compared with other methods [4,9,15–21].

Aqua regia dissolves platinum along with the other elements of spent catalyst such as alumina support, iron, tin, and copper. Precipitation, adsorption, ion exchange, and liquid–liquid separation are some selective separation methods for platinum removal from aqua regia solution [7,10,12,21–39].

As a matter of general practice, the use of synthetic resins for ion exchange and adsorption of precious metal ions leads to a final stage of burning of the synthetic resins to obtain the precious metals in powder elemental form [11,12]. Synthetic resins used for selective separation of precious metals from solution usually contain large amounts of chlorine and nitrogen, and carbon. Hence, upon burning, they produce abnoxious polluting and hazardous gases such as chlorine and nitrogen oxides, and carbon dioxide, a

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proved greenhouse gas. To avoid the utilization of synthetic resins in sorption of metallic ions from solutions because of the environmental drawbacks that was just mentioned, synthesis and application of adsorbents using biomaterials and agricultural wastes have attracted much attention in recent years as an alternative for selective recovery of precious metals from solutions. Biomaterials which contain amine, amid and hydroxyl groups on their surface have demonstrated appreciable affinity to sorption of precious metal ions such as platinum and gold [40–48].

Corn husk is an agricultural waste in maize industry. United States of America, Eastern Europe, Russia, Italy, Brazil and some other countries are main producers of maize in the world. In 2010, about $850 \times 10^6$ metric ton of corn was produced worldwide [49], and maize production in Iran was about $1.8 \times 10^6$ ton in 2010 which meets only about 40% of the current Iran's demand [50].

Residue production by corn plants is roughly equal to the weight of grains produced [51]. Considering the fact that roughly 10% of the corn residues on a dry basis is corn husk, the global production of maize husk was about $85 \times 10^6$ metric ton in 2012 [52]. Maize is produced in different grades worldwide and is mainly used in production of vegetable or cooking oil, starch, processed foods, biofuels, livestock feed and degradable polymers. Currently, corn husk is primarily used in paper industry [53].

Corn husk has a carbonic structure that contains cellulose, hemicellulose, lignin and proteins with hydroxyl, amine and amid groups on its surface, so it can be used to make a selective adsorbent as an environmentally sound alternative to synthetic resins to recover platinum and platinum group metal ions from aqua regia solutions [54–56]. Further, it looks promising that by modification of the structure of waste by certain acids and amines the affinity of the adsorbent for the selective sorption of platinum group metal ions would be enhanced [57,58].

Extensive review of the current literature shows that synthesis of sorbents from natural sources such as agricultural wastes have attracted much attention in recent years (please see 41, 45, 47, and 48, among others). Adsorbents produced from natural sources can be utilized in delicate separation processes. To the best of our knowledge, synthesis of adsorbents from corn husk for separation of platinum ions derived from extraction of spent industrial catalysts has not been reported yet, and fundamentals of adsorption properties of sorbents produced from natural sources is poorly understood. Hence, the main objective of the present study is to prepare and characterize the corn husk adsorbent and examine and study the effectiveness of the prepared adsorbent for selective recovery of platinum ions from model compound media and real solution obtained by aqua regia extraction of an industrial spent alumina support platinum/tin catalyst.

## Experimental

### Materials

Corn husk used in preparation of the adsorbent was obtained from the local market in Isfahan, Iran. It contains organic compounds which evaporate during final sintering procedure of saturated adsorbent, and it has usually about 38.2% cellulose, 44.5% hemicelluloses, 6.6% lignin, 1.9% protein, and 2.8% ash [54,55].

Spent platinum–tin catalyst was obtained from Arak Petroleum Refining Company (Arak, Iran). Detailed elemental analysis of the spent catalyst using XRF analyzer is presented in Table 1. Analytical grade sulfuric acid (95–97%), hydrochloric acid (37%), platinum (II) chloride, diethyl amine, formaldehyde solution, and paraformaldehyde were all from Merck Chemicals Company.

**Table 1**
XRF analysis result of spent catalyst from Arak Petroleum Refining Company.

| Compound | Concentration (wt%) (%w/w) |
|---|---|
| $Al_2O_3$ | 95.82 |
| Cl | 0.386 |
| Pt | 0.35 |
| $SnO_2$ | 0.290 |
| $Fe_2O_3$ | 0.258 |
| CuO | 0.088 |
| ZnO | 0.039 |
| $SO_3$ | 0.020 |
| LOI[a] | 2.75 |
| Total | 100.00 |

[a] Loss on ignition.

### Methods

### Analytical instruments

Inductively coupled plasma optical emission spectrometry (ICP-OES), Optima 7300 DV, ICP-OES instrument, was used for quantitative determination of elements in solution. Powder X-ray diffraction (X-ray Diffractometer Bruker, D8 Advance Germany) was used to determine the possible presence of crystalline structures in the adsorbent and calcination products of adsorbents after the completion of adsorption experiments. X-ray fluorescence (Bruker, S4 PIONEER, Germany) was used to determine the elemental analysis of the spent catalyst and inorganic phase (ashes) of adsorbents. Carbon, hydrogen, nitrogen, and sulfur analysis (CHNS), Elementar Vario EL III, was used to determine the organic phase of the adsorbent samples. FTIR, Tensor 27 from Bruker Company, was used to record the FTIR spectrum and determine the bonds and functional groups on the surface and matrix of the adsorbents. The atomic force microscope (AFM) analysis equipped with ImagePlus 2.9 software for particle size measurement (CSM compact frame from Bruker Company) was used to determine the size distribution of adsorbent particles. The separation of the solid from the liquid phase was carried out by centrifugation at 5000 rpm (Behdad Universal, Model abh-1200, Iran).

### Leaching of the spent catalyst

The spent catalyst was subject to extraction using the regular aqua regia solution method with some minor modifications [12]. The extraction supernatant solution (which here we call it the real or the intact solution) was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES). The results of ICP-OES analysis of the real solution leached out from the spent catalyst using aqua regia solution are listed in Table 2.

### Preparation of Pt model compound reference solution

Model compound media (solution) of platinum ions was prepared as a reference. To this end, 1 g of $PtCl_2$ was dissolved in 100 ml of aqua regia solvent at room temperature and a relatively concentrated solution of platinum ions was prepared.

**Table 2**
Concentration of elements in real solution result from extraction supernatant of spent catalyst by aqua regia.

| Components | Concentration (mg/l) |
|---|---|
| Pt | 140.12 |
| Sn | 0.24 |
| Zn | 0 |
| Fe | 6.58 |
| Cu | 2.85 |
| Al | 16,650 |