Vegetable Sorbents to Extract Iron (II) Ions for Mohr’s Salt Solutions

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Abstract. Heavy-metal pollution is a major problem in towns and cities alike. Vegetable sorbents have been actively researched in recent years as a solution to environmental problems. The Republic of North Ossetia-Alania mainly grows corn and hops. This paper presents the results of using vegetable sorbents (hop cones, corn snouts and cobs) to adsorb iron (II) ions from model solutions of Mohr’s salt (NH₄)₂Fe(SO₄)₂⋅6H₂O. It has been found out that crushed corn cobs do not adsorb iron (II) ions. Hop cones are the best sorbent of the three. Data was used to plot the adsorption isotherms described by the Langmuir equation. The research team calculated the adsorption equilibrium constant as well as the maximum adsorption.

1. Introduction

Adsorption has long been used industrially to separate components, extract impurities, concentrate solutions, and treat industrial wastewaters. Polymer sorbents based on natural, modified, and synthesized materials feature a high adsorption capacity. In recent decades, researchers have shown great interest in the adsorption properties of microorganisms, algae, by-productions or wastes of agriculture and woodworking [1,2]. Adsorption-wise, these materials are on part with their polymer counterparts; on top of that, they are eco-friendly, affordable, and enable integrated waste-free utilization of natural materials. Charcoal is one popular sorbent; researchers have also analyzed the adsorption properties of oak bark and leaves, acorns [3-6], and sawdust [7-12]. Non-wooden plant materials such as oat, rye, and wheat straws; wood, flax, and cotton; chickpea flour; corn, pea, and buckwheat shells and bran; and sunflower glume seem promising for extraction of heavy-metal ions from low-concentration solutions [13-17].

This paper presents the results of using vegetable sorbents (hop cones, corn snouts and cobs) to adsorb iron (II) ions from model solutions of Mohr’s salt (NH₄)₂Fe(SO₄)₂⋅6H₂O. These specific crops were selected because the Republic of North Ossetia-Alania is one of the TOP 10 producers of corn grain [18] with the cultivation of hops on the rise. [19]

2. Research materials and methods

To find the adsorption capacity, 2 grams of dried and crushed materials was placed in 200 ml of freshly made solutions with the following iron (II) ion concentrations: (a) 0.05 g/l; (b) 0.1 g/l; (c) 0.3 g/l; and (d) 0.5 g/l. The mixture was stirred continuously. To reach equilibrium, the solution remained...
in contact with the sorbent for 24 hours. Iron ion concentration was measured by the photocolorimetric method at specific intervals [20]. All the figures below are the averages of three parallel experiments. The collected data has been used to calculate the metal extraction rate $\varepsilon$, % (1) as well as the specific adsorption capacity $A$, mg/g (2) by the formulas:

$$
\varepsilon = \frac{C_0 - C_{\text{равн}}}{C_0} \cdot 100\%
$$

$$
A = \frac{(C_0 - C_{\text{равн}}) \cdot V}{m} \cdot 1000
$$

where $m$ is the mass of the dry sorbent, g

$C_0$ is the concentration of metal in the original solution, g/l

$C_{\text{равн}}$ is the equilibrium (residual) concentration of metal, g/l

$V$ is the volume of tested solution, l [21].

### 3. Results and discussion

The table below presents the values of $\varepsilon$ and $A$ as a function of time for solutions that originally had different iron (II) ion concentrations.

| Sorbent     | $C_0$, g/l | Time, h | 1   | 3   | 6   | 9   | 24  |
|-------------|------------|---------|-----|-----|-----|-----|-----|
| Hop cones   | 0.05       | $64$    | 70  | 74  | 78  | 80  | 84  |
|             | 0.1        | $44$    | 54  | 64  | 70  | 70  | 71  |
|             | 0.3        | $23$    | 8   | 21  | 27  | 33  | 31  |
|             | 0.5        | $12$    | 5   | 25  | 13.5| 37  | 19.5|
| Corn snouts | 0.05       | $72$    | 78  | 78  | 80  | 80  | 90  |
|             | 0.1        | $13$    | 25  | 28  | 28  | 29  | 31  |
|             | 0.3        | $18$    | 5.5 | 7.0 | 15  | 12  | 13  |
|             | 0.5        | $16$    | 22  | 11.1| 18  | 16  | 8.0 |
|             | 0.05       | $18$    | 0.9 | 20  | 1.0 | 33  | 31  |
|             | 0.1        | $16$    | 1.6 | 20  | 2.0 | 30  | 30  |
|             | 0.3        | $7$     | 2.2 | 13  | 4.0 | 6.0 | 16  |
|             | 0.5        | $12$    | 6.2 | 13  | 3.1 | 15  | 7.5 |

Apparantly, hop cones and corn snouts can extract more than 70% of metal cations from a 0.05 g/l solution within 1 to 3 hours. At higher concentrations, the research team observed desorption from the hop cones after three-hour exposure, followed by adsorption. Specific adsorption capacity values make it clear that corn cobs are ineffective sorbents while the low extraction of iron cations was due to the cobs swelling in the solutions.

Analysis of vegetable sorbent kinetics in a static experiment thus shows that hop cones are the best sorbent. The hop-cone adsorption isotherms are classic Type I and Type II curves per the BET theory and follow the Langmuir equation, see Figure [22]. The process begins with monomolecular microporous reversible adsorption with the monolayer saturation $A \approx 7$ mg(Fe$^{2+}$)/g. A longer contact results in polymolecular adsorption.
Figure 1. Hop-cone adsorption isotherms.

The adsorption equilibrium constant $b$ and the maximum adsorption $A_\infty$ have been calculated per the Langmuir equation written as

$$\frac{1}{A} = \frac{1}{A_\infty} + \frac{1}{A_\infty b C_0}.$$  \hspace{1cm} (3)

For hop-cone absorption, $A_\infty = 7.7 \text{ mg/g}$, $b = 14.43$. The high value of $b$ indicates a strong intermolecular interaction between hop cones and iron (II) cations, while the sorbent pore size matches that of the adsorbate.

4. Conclusions
1. Hop cones are strong at adsorbing iron (II) cations from Mohr’s salt solutions.
2. Corn snouts can be used for adsorption only from weak solutions; even that will require prolonged exposure (> 6 hours).
3. Corn cobs do not adsorb iron (II) ions.

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