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SEARCH FOR NEW AFFORDABLE SORBENTS FOR PROTECTION OF WATER RESERVOIRS FROM POLLUTION

Dmytro KOROBİY, Oleksandr KHOKHOTVA

Igor Sikorsky Kyiv Polytechnic Institute

37, Prospect Beresteiskyi, Kyiv, 03056, Ukraine

e-mail: dkorobiy@gmail.com

Abstract

Pollution of water bodies in the world causes a growing need to find new, effective, selective, affordable and environmentally friendly sorbents for the removal of pollutants. Analysis of existing research emphasizes the importance of developing both highly effective and cheap, non-toxic and easily renewable sorbents. Natural materials, such as lignocellulosic sorbents (e.g. sawdust) and mineral ones, are promising in this regard. Among these natural materials, sawdust has its advantages as a waste of the woodworking industry, which makes its use convenient and economically profitable. Natural raw materials do not always have the desired sorption properties. However, they can be improved by modifying the surface with various functional groups. Research and development of methods for purifying water bodies from heavy metals, such as copper, are particularly important, since this metal can pollute natural water resources through industrial use and, as a result, accumulate over time in the body. To date, the use of modified lignocellulosic sorbents, in particular pine sawdust, for water purification from heavy metals has not been sufficiently studied. In this regard, in the study, it was decided to study the sorption properties of pine sawdust modified with urea and ammonium phosphate, since these reagents are able to generate functional groups with nitrogen and phosphorus, which can retain d-metal ions, in particular copper. The process of modifying pine sawdust included the following stages: sawdust samples were filled with solutions of ammonium phosphate and urea of appropriate concentration, settled, dried in air, calcined in a drying oven, washed with hot distilled water to neutral pH and dried to constant mass. The sorption properties of modified sawdust were studied by determining the change in the concentration of a 2 mM copper (II) sulfate solution before and after sorption, and the concentration of Cu^{2+} ions was determined by the back titration method. Before titration, the pH of the solutions after sorption was also measured.

Keywords: water purification, sorption properties of pine sawdust, sawdust modification, modification with urea and ammonium phosphate.

With the development of industry in the world, the relevance of cleaning water bodies from pollution is becoming increasingly significant, both because of the harmful effects on human health and because of the growing economic costs of controlling and restoring aquatic environments [1, 2]. Not the least role in these issues is played by the threat of "invisible pollutants", which are resistant to traditional water purification methods and can become increasingly toxic, affecting aquatic ecosystems and human health [3]. All this leads to the need to find more effective and selective sorbents capable of removing pollutants from low-concentrated solutions of various nature and at the same time affordable and cheap.

Having analyzed the known studies of various sorption materials for possible water pollutants, we see that in addition to the development of new effective and highly selective sorbents, the issue of developing relatively

cheap, non-toxic and easily renewable sorbents is also important. Among such materials, one can note the use of natural sorbents, for example, lignocellulosic, such as sawdust, as well as various mineral sorbents. Speaking of sorption by natural sorbents, one can also cite as an example the ability of Ukrainian kaolinite clay to purify water from nickel, due to its sorption properties [4]. It is also worth noting that the purification of water bodies using kaolinite clay is especially important for practical application in conditions of economic constraints, taking into account the availability of the material. However, if we compare sawdust and mineral or other natural sorbents, the advantage of sawdust is that its use is quite convenient and promising, both from the point of view of economy, since it is waste from the woodworking industry, and in terms of secondary processing of raw materials.

Naturally, natural raw materials do not always have the desired sorption properties or high efficiency in relation to the components required for the extraction from water. However, such properties or efficiency can be improved by modifying the surface with various functional groups-modifiers.

Among other pollutants that can enter aquatic ecosystems, no less important today is the research and development of methods for purifying water bodies from heavy metals (metals that are poorly excreted from the body and, accordingly, accumulate over time), or metals that can be used as a material for process water pipes at any enterprise, but the increase in their content in natural water resources will also be considered pollution. Among such metals, copper is common, which is also a heavy metal and, due to its resistance to corrosion, can be used for the production of water pipes (for example, cooling systems).

Having analyzed the current experience on the problems of sorption of various pollutants of water bodies by various materials, it is clear that the areas of using natural raw materials for sorption of heavy metals, in particular copper as a frequently used material for water mains in industry, as well as the use of modified lignocellulose sorbents for water purification from inorganic pollutants, in particular heavy metals, remain understudied. In this regard, we decided to investigate the sorption properties of pine sawdust modified with urea ($\text{CO}(\text{NH}_2)_2$) and ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), - reagents that are capable of generating functional groups with nitrogen and phosphorus, which have the potential to retain d-metal ions, due to the formation of stable complexes with them [5, 6].

The process of modification of pine sawdust was carried out as follows. To modify the sawdust, a series of solutions with ammonium phosphate and urea were prepared in the concentration range of 0–0.5 M for $(\text{NH}_4)_3\text{PO}_4$ and 0–2.0 M for $\text{CO}(\text{NH}_2)_2$. Each individual sample of sawdust was filled with the appropriate modifying solution and left to settle. After drying the obtained samples in air and calcining in a drying oven, they were washed on a filter to neutral pH with hot distilled water. After that, the samples were dried to constant mass.

The study of the sorption properties of the modified sawdust samples was carried out by determining the change in the concentration of 2 mM aqueous solution of copper (II) sulfate (CuSO_4) before and after sorption. The concentration of Cu^{2+} ions was determined by the back titration method. Before titration, the pH of the solutions after sorption of Cu^{2+} ions and 2 mM copper (II) sulfate solution used to study the sorption properties of the modified sawdust was measured. The table 1 below shows the results of studies on the sorption of Cu^{2+} ions by modified sawdust.

After analyzing the results of the sorption of modified sawdust, it is clear that for the modification of pine sawdust, ammonium phosphate solutions are better to use with a concentration 3-4 times lower than the urea concentration.

The ratio of urea:ammonium phosphate = 3-4 for pine sawdust modification resulted in higher efficiency of copper removal. Higher concentrations of modification solutions possibly promoted higher level of introduction of N and P into cellulosic material. Heavy metal can be retained in lignocellulose by several mechanisms, mainly ion exchange and complexation. Higher N and P content in pine sawdust is revealed in lower pH drop after sorption with simultaneous low residual copper concentration.

able 1. The results of studies on the sorption of Cu²⁺ ions by modified sawdust

Concentration of modifying solution and main parameters studied	Name of the modified sawdust sample										2 mM CuSO ₄ solution **
	00*	1	2	3	4	C0	C1	C2	C3	C4	
C _M ((NH ₄) ₃ PO ₄)	0	0,2	0,3	0,4	0,5	0,5	0,5	0,5	0,5	0,5	-
C _M (CO(NH ₂) ₂)	0	0,5	1,0	1,5	2,0	0	0,5	1,0	1,5	2,0	-
Concentration of Cu ²⁺ ions after sorption, mg/l	89,0	17,5	2,4	0,8	0,8	35,0	33,4	15,9	0,8	0,8	135,0
% sorbed ions Cu ²⁺	34,1	87,1	98,2	99,4	99,4	74,1	75,3	88,2	99,4	99,4	-
pH of solutions after sorption of Cu ²⁺ ions	3,99	3,31	3,31	3,57	3,73	2,90	3,01	3,26	3,56	3,73	5,22

* – the name "00" corresponds to distilled water, without modifying reagents, as a blank sample.

** – 2 mM aqueous solution of copper (II) sulfate used for sorption studies; the results in this column are given for comparison with the sorption properties of samples of modified pine sawdust.

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ПОШУК НОВИХ ЕКОНОМІЧНО ДОСТУПНИХ СОРБЕНТІВ ДЛЯ ЗАХИСТУ ВОДОЙМ ВІД ЗАБРУДНЕНЬ

Дмитро КОРОБІЙ

Київський політехнічний інститут імені Ігоря Сікорського

пр. Берестейський, 37, м. Київ, 03056, Україна

<https://orcid.org/0009-0007-7039-5721>

Олександр ХОХОТВА

Київський політехнічний інститут імені Ігоря Сікорського

пр. Берестейський, 37, м. Київ, 03056, Україна

<https://orcid.org/0000-0002-2607-9242>

Анотація

Забруднення водойм у світі зумовлює все більшу потребу в пошуку нових, ефективних, селективних, доступних та екологічно безпечних сорбентів для вилучення забруднювачів. Аналіз існуючих досліджень підкреслює важливість розробки як високоефективних, так і дешевих, нетоксичних та легко відновлюваних сорбентів. Природні матеріали, такі як лігноцелюлозні сорбенти (наприклад, тирса) та мінеральні є перспективними в цьому плані. Серед цих природних матеріалів тирса має свої переваги, як відхід деревообробної промисловості, що робить її використання зручним та економічно вигідним. Не завжди природна сировина має бажані сорбційні властивості. Однак їх можна покращити шляхом модифікації поверхні різноманітними функціональними групами. Дослідження та розробка методів очищення водойм від важких металів, таких як мідь, є особливо важливими, оскільки цей метал може забруднювати природні водні ресурси через промислове використання і, як наслідок, накопичуватися з часом в організмі. На сьогоднішній день ще недостатньо досліджено використання модифікованих лігноцелюлозних сорбентів, зокрема соснової тирси, для очищення води від важких металів. У зв'язку з цим, у дослідженні було вирішено вивчити сорбційні властивості соснової тирси, модифікованої сечовиною та амоній фосфатом, оскільки ці реагенти здатні генерувати функціональні групи з нітрогеном та фосфором, які можуть затримувати йони d-металів, зокрема міді. Процес модифікації соснової тирси включав такі етапи: зразки тирси заливали розчинами амоній фосфату і сечовини, відповідної концентрації, відстоювали, висушували на повітрі, прожарювали у сушильній шафі, промивали гарячою дистильованою водою до нейтрального рН та сушили до постійної маси. Сорбційні властивості модифікованої тирси досліджували шляхом визначення зміни концентрації 2 мМ розчину купрум (II) сульфату до та після сорбції, а концентрацію йонів Cu^{2+} визначали методом зворотного титрування. Перед титруванням також вимірювали рН розчинів після сорбції.

Ключові слова: очистка водойм, сорбційні властивості соснової тирси, модифікація тирси, модифікація сечовиною та амоній фосфатом.