Influence of the nature of the binding material on properties of the sorbents

Y Smyatskaya¹, N Politaeva¹, A Chusov¹

¹Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya str., 195251, Saint-Petersburg, Russia

Makarova.yulia169@mail.ru

Abstract. This article discusses sorbents for water purification from heavy metals and petroleum products made from cheap materials such as agricultural waste, industrial waste, sawdust, sheet litter, and others. Literary data in which it is proposed to modify the waste to improve the physic-chemical and sorption characteristics. Acids, alkalis, salts, alcohols, and organic compounds are used as reagents. Additive to the sorption material of the polymer binder allows obtaining material of this form. This article proposes to manufacture sorbents from cotton waste and agricultural waste (wheat husk). Preliminary heat treatment of materials allows developing a specific surface area and obtaining new functional groups, thereby increasing the cleaning efficiency of model solutions from heavy metal ions (zinc, cadmium, lead, copper). The authors propose sorbents to be laid in layers in the polymer case and thus a three-layer filter “СОМ” was manufactured. To give the filter a frame structure, it is proposed to introduce polymeric binders (phenol-formaldehyde resins, adhesives, paraffin, a polymeric matrix). Considered 3 types of filters that differ in the content of the polymer matrix. The polymer matrix consists of phenol, formaldehyde, and sulfuric acid. The highest sorption capacity was observed for the СОМ sample and ranged from 0.88 to 0.90 mg/g, while the cleaning efficiency was up to 89% for zinc ions. Microstructural studies of the samples showed that the introduction of binding additives "smears" the pores and reduces the sorption activity. The introduction of the polymer matrix allows you to save the sorption properties due to the ion exchange mechanism.

1. Introduction

The competent design of the sewerage system from industrial enterprises allows to extend the service life of sewer facilities. Sewerage network, pumping stations, and facilities for cleaning shop floor drains that are placed at the industrial site, refer to the system on-site sewage enterprises. Wastewater discharge from the territory of industrial enterprises is often carried out on a separate sewerage system, i.e. rainwater and industrial fused separately. For some enterprises with appropriate technical and economic justification can be accepted sewage system [1, 2, 3, 4]. It is possible to prevent pollutants from entering the General sewage system by means of local wastewater treatment systems based on different methods: chemical, physic-chemical and biological [5, 6, 7]. One of the most effective methods is the sorption method of wastewater treatment, which allows removing ions of heavy metals. Various materials (activated carbons, zeolite, silica gel, peat) are used as sorbents and find applications in various technological solutions [8, 9, 10]. Ash is used for effective removal of lead, cadmium, copper, and zinc from polluted water [11].
In recent years, much attention has been paid to the use of low-cost adsorbents from plant waste to remove Cu (II) and Zn (II) from polluted waters. In article [12] sorption characteristics of two types of the wastes received as a result of agriculture are studied: soy bran and mustard husk. The influence of contact time, initial concentration of metal ions, pH, sorbent mass, and temperature on the adsorption capacity of materials as sorbents is investigated. Article [13] describes the use of olive seeds for the extraction of iron, lead, copper.

There is a large variety of sorption materials on the market for the treatment of waste water from heavy metals and petroleum products. Sorbents are created on the basis of active carbons, natural materials, carbon sorbents and nanomaterials. However, the most promising and cost-effective sorbents made from recycled materials. These materials allow us to solve two problems at once: water purification and waste disposal. Because of the availability and low cost, sorbents based on the waste of the agro-industrial complex attract scientists from many countries. A large number of works aimed at studying the use of agricultural waste [14, 15], industrial waste, and others [16] as sorption materials. However, in its pure form, the use of such sorbents is often technically very difficult, therefore, work aimed at creating composite materials is very relevant [17].

Scientists propose to use hydrophobized sawdust as sorbents for wastewater from petroleum products. Hydrophobization was carried out with paraffin, which, it is proposed to isolate from oil sludge - oil refining waste [18].

Waste agricultural production buckwheat husks are used in combination with polyurethane foam. The composite material is used to collect oil, petroleum products, and oils. Introduction to the material up to 45% buckwheat husk allows you to get a sorbent with hydrophobic and oleophilic characteristics [19].

The authors of [20] propose to use a sintered composite filter, obtained by self-pressing of thermally expanded graphite waste and polyacrylonitrile fibers during heat treatment at a temperature of 450°C. These filters have high sorption properties with respect to petroleum products and heavy metal ions.

In the production of Cellesorb series sorbents, various waste products from the pulp and paper, woodworking, and textile industries were used, where chemical fibers were used as a binder. The characteristics of these sorbents are not inferior to modern analogs [21].

The use of a binder simplifies the technical difficulties of using such bulk sorbents as husks of wheat, millet, sunflower, etc., but reduces their sorption properties. Therefore, it is advisable to use a polymer matrix that has sorption properties.

In the works of M.M. Kardash describes the technology of manufacturing a unique chemisorption fibrous material from polyacrylonitrile fibers and a polymeric binder (phenol-formaldehyde matrix). "PolikonA" with the properties of ananites and "PolikonK" with the properties of cation exchangers. In this material, the polymer matrix has chemisorption properties [22].

When choosing a material for the extraction of heavy metals from wastewater, the content of lignin and cellulose plays an important role. A large amount of 80-95% cellulose is contained in cotton waste (cotton waste) [23]. Besides, to enhance the potential of functional groups and increase the number of active groups, it is advisable to pretreat the material with various modifying agents. Organic and mineral acids (HCl, HNO₃, H₂SO₄, acetic acid, citric acid, and formic acid), bases, and salts (NaOH, Na₂CO₃, Ca(OH)₂ and CaCl₂), oxidizing agents (H₂O₂ and K₂MnO₄), organic are used as modifiers. compounds (aldehydes, CH₃OH) and others. In the works of Finnish scientists studied the modification of peat and sawdust with hydrochloric and citric acid [24].

Turkish scientists have studied the use of tea waste as a biosorbent. The optimum pH and temperature were selected for the extraction of copper and nickel ions, which were 5 and 50°C, respectively. Pre-waste of tea was washed and dried in an oven at a temperature of 105°C. The sorption capacity for nickel ions of 10.8 mg/g and copper ions of 14.9 mg/g was achieved [25, 26].

Known work [27, 28], in which it is proposed to use as a sorbent feather of Dromaius novaehollandiae were collected from poultry and chitosan. As a result of this technology, it is possible to obtain a biopolymer composite having a sorption capacity of 70.42 mg/g).
Coffee grounds are cheap sorption material for the treatment of wastewater from lead and fluoride [16]. The exhausted coffee grounds gathered from industrial wastes have been acid-activated and examined for their adsorption capacity. The surface morphology and elemental characterization of pre- and post-adsorption operations by spectral analysis confirmed the potential of the exhausted coffee ground as a successful bio-sorbent. However, the thermodynamic analysis confirmed the adsorption to be spontaneous physisorption with Langmuir mode of homogenous monolayer deposition. The kinetics of adsorption is well defined by the pseudo-second-order model for both lead and fluoride. A significant quantity of lead and fluoride is removed from the synthetic contaminated water by the proposed bio-sorbent with the respective sorption capabilities of 61.6 mg/g and 9.05 mg/g.

For the extraction of nickel (II) ions from aqueous media, a chitosan-based biopolymer coated with a layer of calcium and silicon alginate is effective. The adsorption of metal ions depends on the amount of adsorbent, the concentration of metal ions, the time of mixing, and the pH of the solution. The maximum cure efficiency of nickel (II) ions was found at pH 5.0. The adsorption equations were well correlated by the Langmuir equations and the Freundlich isotherm. The maximum sorption capacity was 254.3 mg/g for a chitosan-based biosorbent coated with a silicon layer [29].

The purpose of this study is to study the influence of the nature of the binder on the sorption properties of sorbents from agricultural waste.

The objects of the study are agricultural waste and sorbents based on them with various binders (Phenol-formaldehyde resin, paraffin, glue BF, polymer matrix).

The research objectives include:
- the creation of sorbents from agricultural waste and binders
- study of the sorption properties of the obtained sorbents
- study of the influence of the binder material on the physicochemical properties of the obtained sorbents

2. Methods

Heat treatment of sorption materials was carried out in a special steel form. The optimal conditions for the thermal activation of sorbents, the temperature of which was 350°C - for wheat husk for 20 minutes and 450°C for cotton waste (CW) within 8 min.

For the manufacture of a three-layer filter (COM), sorbents were layered in layers in a special casing made of polymeric material so that the outer layers contained cotton-containing waste and the inner one contained cellulosic waste, with the following ratio of components, mass %: cotton-containing waste 20%; cellulose waste 80%.

For the preparation of the composite material, a binder of different composition was injected and mixed with thermally activated waste in the ratio: 20% - bond, 80% - wheat husk, thermally activated. Then within 24 hours the composite material hardened in a special form.

**Composition of composite materials:**

Filters «COM» of various compositions were prepared.

As a binder material was used:

1. Phenol-formaldehyde resin - synthetic resin, a product of phenol polycondensation with formaldehyde. With its use was obtained composite material "COM-1"

2. Paraffin - a mixture of aliphatic saturated hydrocarbons (alkanes) of composition from \( C_{18}H_{38} \) to \( C_{35}H_{72} \). Used as a hydrophobic and binding reagent, with this was obtained a composite material "COM-2".

3. Glue BF - in the composition, which includes polyvinyl butyral, dibutyl phthalate dissolved in ethanol. When it was used, the composite material COM-3 was obtained.

4. Polymer matrix (90%) + heat-treated CW (10%) composite material "COM- X "was obtained;

5. Polymer matrix (75%) + heat-treated wheat husk (25%) - composite material "COM-II" was obtained;

6. Polymer matrix (60%) + heat-treated wheat husk (20%) + heat-treated CW (20%)-composite material "COM-XII" was obtained;
The obtained composite materials in the amount of 1 g were added to 100 ml of model wastewater containing in the mixture a heavy metal ion (IHМ) of cadmium, lead, and copper with an initial concentration of 10 mg/l. The residual concentration was determined by the voltamperometric method on the device AKB-07 MK. The measurements were carried out according to certified methods of Russian Standart 14.1: 2: 4.69-96 by the method of inversion voltammetry. The cleaning efficiency (E) of model solutions was calculated using the final (С fin) and initial (Сi) concentrations:

\[ E = \left(\frac{C_i - C_{fin}}{C_i}\right) \times 100\% \]  

(1)

The calculation of the sorption capacity (A) was carried out according to the formula (1) and the results are presented in Table 1.

\[ A = \frac{C_o - C_e}{m} \times V \]  

(2)

Where q is the sorption capacity, \(C_o\) and \(C_e\) are the initial and final concentrations of heavy metals in the solution, \(V(l)\) is the volume of solution and \(m (g)\) is the waste amount.

Microscopy was performed using a raster ion-electron microscope QUANTA 200 3D. At least 3 measurement results were obtained that were statistically processed.

3. Result and Discussion

A composite filter “COM” was developed on the basis of weaving production waste - cotton waste (WC) and wheat husk. Heat treatment provides limited access to oxygen, which allows to obtain materials with a porous structure and to achieve the appearance of soot-graphite compositions. A carbonized layer with high sorption properties is formed on the surface of the heat-treated waste. From the heat-treated waste produced a three-layer filter “COM”. The outer layers provided a solid framework for cellulosic waste and when filtering wastewater they were not entrained in the liquid. This filter has a high cleaning efficiency from ions of heavy metals and petroleum products, but it has a significant drawback, an unstable, constantly changing structure, and a sorption surface in the cleaning process.

Composite filters with the rigidly fixed structure are more reliable in operation, which will be ensured by the addition of binding components.

In the manufacture of a composite material as a binder, we used paraffin, wax, dibutyl phthalate, pine gum, starch, gelatin, carboxymethylcellulose, and a polymer matrix made using a unique technology. From the literature data it is known that the amount of binding additive should not exceed 20-30% to minimize the processes of loss of sorption capacity.

Phenol, formaldehyde and sulfuric acid were used to form the cationic polymer matrix. Materials with sorption properties were obtained by the technology of polycondensation filling, which allows forming materials with high ion-exchange properties. Composite materials were created on the basis of the polymer matrix [22].

Starch, gelatin, carboxyl methylcellulose was also used as binding components. The use of these components leads to the formation of very fragile samples, which are scattered under light pressure, so their further study is not advisable.

Composite filters have been studied for the ability to extract heavy metal ions. The calculation results are given in Table 1.

Adding binders to sorption materials leads to an increase in mechanical strength, but a decrease in the efficiency of wastewater treatment. One of the reasons for this result is the deformation of the sorbent flakes during mechanical mixing with the binder and the subsequent formation of granules, which leads to the partial destruction of the pores in the sorbent and, accordingly, to a decrease in its
active surface. Another reason for the decrease in the sorption capacity of the sorbent during granulation is the insufficient intergranular or interchlopous porosity of the granules.

Table 1. Effectiveness of wastewater treatment from ITM composite materials based on various binder, wheat husk, and cotton waste, $Ci = 10$ mg/l

| Metall             | $C_{fin}$. mg/l | $E$. %  | $A$. mg/g |
|-------------------|-----------------|---------|-----------|
| «COM-1»
| Cadmium (Cd$^{2+}$) | 6.54±1.57       | 34.6±8.3 | 0.35      |
| Lead (Pb$^{2+}$)  | 5.05±1.21       | 49.5±11.9 | 0.50      |
| Cooper (Cu$^{2+}$) | 9.08±2.18       | 9.2±2.2  | 0.10      |
| «COM-2»
| Cadmium (Cd$^{2+}$) | 9.51±2.28       | 4.9±1.2  | 0.05      |
| Lead (Pb$^{2+}$)  | 9.89±2.37       | 1.1±0.3  | 0.01      |
| Cooper (Cu$^{2+}$) | 10.00±2.40      | 0          | 0         |
| «COM-3»
| Cadmium (Cd$^{2+}$) | 6.48±1.56       | 35.2±8.4  | 0.35      |
| Lead (Pb$^{2+}$)  | 8.93±2.14       | 10.8±2.6  | 0.11      |
| Cooper (Cu$^{2+}$) | 8.04±1.92       | 19.6±4.7  | 0.20      |
| «COM-4»
| Cadmium (Cd$^{2+}$) | 8.25±1.98       | 17.5±4.2  | 0.18      |
| Lead (Pb$^{2+}$)  | 9.99±2.40       | 1.2±0.3   | 0.002     |
| Cooper (Cu$^{2+}$) | 9.00±2.16       | 10.0±2.4  | 0.1       |
| «COM-5»
| Cadmium (Cd$^{2+}$) | 7.11±1.70       | 29.0±7.0  | 0.29      |
| Lead (Pb$^{2+}$)  | 7.05±1.69       | 29.5±7.1  | 0.30      |
| Cooper (Cu$^{2+}$) | 7.77±1.86       | 22.4±5.4  | 0.22      |
| «COM-6»
| Cadmium (Cd$^{2+}$) | 5.90±1.42       | 40.9±9.8  | 0.41      |
| Lead (Pb$^{2+}$)  | 5.06±1.21       | 49.3±11.8 | 0.49      |
| Cooper (Cu$^{2+}$) | 7.63±1.83       | 23.7±5.7  | 0.24      |
| «COM-7»
| Cadmium (Cd$^{2+}$) | 1.19±0.29       | 87.1±20.9 | 0.88      |
| Lead (Pb$^{2+}$)  | 0.98±0.24       | 88.3±21.2 | 0.90      |
| Cooper (Cu$^{2+}$) | 1.06±0.25       | 89.0±21.4 | 0.89      |

COM as binder phenol-formaldehyde resin; $^2$COM as binder paraffin; $^3$COM as binder glue $BF$; Polymer matrix (90%) + heat-treated cotton waste (10%); $^5$Polymer matrix (75%) + heat-treated wheat husk (25%); $^6$Polymer matrix (60%) + heat-treated wheat husk (20%) + heat-treated cotton waste (20%); $^7$COM

The introduction of a binder material partially clogs the pores and, therefore, a decrease in the sorption capacity. This is confirmed by microstructural studies of the surface morphology of the samples. When microcopying in combination with a large depth of field, characteristic of raster electron microscopes, the use of this method allows you to explore the shape, size of particles, the degree of their agglomeration and study the morphology of the surface of materials (Figure 1). The study of the morphology of the heat-treated wheat husk shows the presence of a highly porous surface (Fig. 1, b), when using the binder components, the sample pores become clogged and the sorption capacity decreases (Figure 1 c, d).
Composite material "COM-XP", made on the basis of the polymer matrix showed higher sorption properties, as compared with other studied materials. This is most likely due to the ion-exchange properties of the polymer matrix itself.

Since the introduction of a binder additive significantly reduces the sorption properties of the material, it is proposed to abandon the additive and place sorption materials in the polymer case and use them as a composite filter.

As a result of the work done, it was shown that the composition of the binder additive, in the manufacture of composite sorption materials from the waste of the agro-industrial complex, affects the sorption properties [30-32]. The introduction of a binder material reduces the sorption capacity by reducing its active surface, as evidenced by microstructural studies. It is advisable to use as a binder polymer matrix, which has chemisorption properties or a composite filter without a binder additive.

4. Conclusion
1. Sorption filters of various compositions were made on the basis of heat-treated waste - cotton-containing fiber and wheat husk. As a binding component, phenol-formaldehyde resin "COM-1", paraffin "COM-2", adhesive BF "COM-3" are used.
2. Sorption filters based on a polymer matrix were made:
   - “COM-X” - polymer matrix (90%) + heat-treated HSV (10%)
   - “SOM-P” - polymer matrix (75%) + heat-treated wheat husk (25%)
“SOM-XP” - polymer matrix + heat-treated wheat husk (20%) + heat-treated CW (20%).
3. For the filter “COM” the highest sorption properties were obtained - $E = 89\%$, $A = 89\, \text{mg/g}$ for zinc ions. The disadvantage of this filter is the difficulty in operation.
4. For practical use the «COM» sorption filter is recommended ($E = 49\%$, $A = 0.49\, \text{mg/g}$).

References
[1] Galkin U A 2012 Development of a sewage treatment system for storm and industrial sewers in large cities and industrial enterprises Bulletin of SASAS Urban planning and architecture 4(8) pp 64-70
[2] Chechevichkin V N, Vatin N I 2014 Specifics of surface runoff contents and treatment in large cities Magazine of Civil Engineering 50 (6) pp 67-74
[3] Molokov M V and Shifrin V N 1977 Surface runoff cleaning from the territories of cities and industrial sites M, Stroyizdat
[4] Kuznetsov E P, Dybov A M, Sutyrin N M, and Chusov A N 2016 Engineering support and equipment of objects of urban construction and economy.-SPb Publishing house Polytechnic University
[5] Chechevichkin V, Vatin N 2014 Megacities land drainage and land runoff features and treatment Features and methods of wastewater treatment Applied Mechanics and Materials. pp 641-642 pp 409-415
[6] Molodkina L M 2010 Methods of purification of drinking, natural and wastewater a training manual SPb Publishing house of the Polytechnic University
[7] Filatov E G 2015 Overview of wastewater treatment technologies from heavy metal ions based on physicochemical processes News of universities Applied Chemistry and Biotechnology 2 (13) pp 97-109
[8] Vukoевич Medvidovich, Dakovich A, Ugrina M, Trgo M Nuich I and Markovich M 2017 Evaluation of low-cost sorbents as potential materials for on-site purification of water contaminated with heavy metals Technologica Acta 10(2) pp 9–13
[9] Chechevichkin AV, Vatin NI, Samonin V V and Grekov MA 2017 Purification of hot water by zeolite modified with manganese dioxide Magazine of Civil Engineering 76(8) pp 201-213
[10] Vatin N I, Chechevichkin V N, Chechevichkin A V, Shilova Y and Yakunin LA 2014 Application of natural zeolites for aquatic and air medium purification Applied Mechanics and Materials pp 587-589 pp 565-572
[11] Harja M, BuemA, Mircea D, Sutiman and Cretescu I 2013 Removal of heavy metal ions from aqueous solutions using low-cost sorbents obtained from ash Chemical Papers 67 (5) pp 497–508
[12] Humelniciu D, Ignat M and Doroftei F 2015 Agricultural by-products as low-cost sorbents for the removal of heavy metals from dilute wastewaters Environ Monit Assess pp 187–222
[13] Alslaili T M, Abustan I, Ahmad M and Foul A 2014 Kinetics and equilibrium adsorption of iron (II) lead (II) and copper (II) onto activated carbon prepared from olive stone waste Desalination and Water Treatment 52 pp 7887–7897
[14] Sabino De Gisi, Giusy Lofrano, Mariangela Grassi, Michele Notarnicola 2016 Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment A review Sustainable Materials and Technologies 9 pp 10-40
[15] George N I, Kyzas Z 2014 Green Adsorbents for Wastewaters A Critical Review Materials 7(1) pp 333-364 DOI:10.3390/ma7010333
[16] Ungureanu G, Santos S, Boaventura R and Botelho C 2015 Arsenic and antimony in water and wastewater overview of removal techniques with special reference to latest advances in adsorption J Environ Manag 151 pp 326–342 DOI: 10.1016/j.
[17] Politaeva N, Taranovskaya E, Slugin V and Prokhorov V 2017 Technology of Obtaining Composite Sorbents for Water Purification J Chem Eng Process Technol 8 pp 3-5 DOI: 10.4172/2157-7048.10003385
[18] Pashajan A, Nesterov A V and Isakova A V 2008 The patent 2332359 Russian Federations МПК With 02 F 1/140 Way of sewage treatment from oil and oil products ГОУВПО Bryansk st Technical academy It is published Inventions Has got Models

[19] Schepakin M B, Gafurov I G, Mishulin G M and Israfilov I H 2000 The Ecologo-technological complex for clearing of hydrosphere of oil and oil products Ecology and the industry of Russia 11 pp 40-43

[20] Sobgaida N A, Nikitina T V and Olshanskaya L N 2008 Fibrous and carbon materials for sewage treatment from oil products Chemical and oil and gas mechanical engineering 1 pp 33-34

[21] Skorodumov A N, Kuchin G P and Guschin A E 2008 Manufacture of sorbents from a waste and their use for clearing of drains Manufacture Ecology 6 pp 64-65

[22] Kardash M M, Fedorchenko N B, Fedorchenko A A 2003 Problems of wastewater treatment and methods for solving them Chemical fiber 5 pp 32-40

[23] Abdolalia A, Guoa W S, Ngoa H H, Chenb S S, Nguyenb N C and Tunge K L 2014 Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment A critical review Bioresource Technology 160 pp 57-66

[24] Gogoi H 2018 Removal of metals from industrial wastewater and urban runoff by mineral and bio-based sorbents J Environmental Management 1 209 pp 316-27 DOI: 10.1016

[25] Sukru A, Sayiter Y, Mustafa O and Ayben P 2016 Adsorption of Heavy Metals Onto Waste Tea European Scientific Journal 11 pp 1-7

[26] Meenakshi Nandal, Rajni Hooda and Geeta Dhania 2014 Tea Wastes as a Sorbent for Removal of Heavy Metals from wastewater International Journal of Current Engineering and Technology 4 pp 243-247

[27] Anantha Ratna Kumari, Kota 2016 Sobha Removal of lead by adsorption with the renewable biopolymer composite of feather (Dromaius novaehollandiae) and chitosan (Agaricus bisporus) Environ Technol Innov pp 6-8

[28] Naga Babu A 2018 Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent J Environmental Management pp 218-219

[29] Vijaya Y 2008 Modified chitosan and calcium alginate biopolymer sorbents Carbohydrate Polymers 72 pp 261–271

[30] Sobgaida N, Olshanskaya L and Makarova Yu 2009 Wastewater treatment from heavy metal ions using sorbents - waste from the woodworking and agricultural industries Chemical and oil and gas engineering 9 pp 43-45

[31] Sobgaida N A, Olshanskaya L N and Makarova Yu A Cleaning petroleum products from waste water with composite filters based on waste products Chemical and Petroleum Engineering 46 (3) pp 171-177 DOI: 10.1007/s10556-010-9313

[32] Sobgaida N A, Ol'shanskaya L N and Makarova Yu A 2009 Removing heavy-metal ions from effluents by means of sorbent formed from wood-working and agribusiness wastes Chemical and Petroleum Engineering 45(9-10) pp 580-584 DOI: 10.1007/s10556-010-9241-9