Purification of aqueous media from toxicants carbon-mineral sorbent

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Abstract. To purify aquatic environments from various toxicants, we obtained a carbon-mineral sorbent from the reed stems of the South (Phragmitesaustralis) by carbonization. At the stage of carbonization of the crushed reed, a carcass, containing carbon and silicate constituents, is formed. Depending on the type of feedstock and the carbonization temperature of the organic component, the content of the silicate component varies in the range of 20-30%. The process is carried out until a sorbent containing 70-80% of the carbon component, 29-19% of the silicate component and 1% of water is obtained. The adsorption capacity of the obtained carbon-mineral sorbent towards medium and macromolecular organic compounds, and heavy metals was studied. As a result, it was established that the carbon-mineral sorbent obtained from the reed stems of the South (Phragmitesaustralis) has moderately distributed sizes of macro- and micropores. The presence of two constituents, carbon and silicate, in the structure of the obtained sorbent promotes the sorption of phenols, hydrocarbons, barbiturates, cholesterol derivatives, aminoglycosides, anthracyclines and other compounds, as well as ions of heavy metals, which makes it possible to use a sorbent in the chemical industry for purification of sewage, natural waters and it can be proposed for the purification of biological fluids.

1. Introduction

Water resources are one of the main components of ensuring life on earth. The water which doesn’t contain toxic impurity (petrochemicals, phenols, ions of heavy metals) is necessary to maintain the vital processes of living organisms. As it is known, in natural reservoirs – the rivers, lakes, ponds, the liquid cleanses itself naturally, but this process is very long, while aerobic organisms play an important role in wastewater treatment. To ensure the protection of water resources from depletion, the norms for discharging sewage fluids of different categories into the reservoirs are legally fixed in Russia.

The struggle against pollution of the water basin is carried out in three main directions:
1) creation of new technological processes based on a without waste principle,
2) improvement of technological processes that allow eliminating or reducing the release of toxic substances into water sources, and
3) processing of superficial drains with objective of extraction of impurity and their further use or neutralization of their harmful influence on an environment.
To provide an ecological security it is possible to use different methods of purification. Mechanical or physical, it is applied as preliminary. In the process of mechanical purification of water, undissolved impurities are removed from it by straining, filtering and settling, the cleaning range in which the mechanical methods of sewage purification help to purify water is quite wide. At clearing household sewage up to sixty percent of impurity maybe removed from water, and in case of clearing industrial sewage – up to ninety percent of impurity maybe removed from water by means of mechanical methods of sewage treatment.

In addition, it is important to understand that mechanical methods of wastewater treatment, being in fact the cheapest among other methods of purification, are designed to prepare wastewater for participation in chemical and biological treatment processes. Large dispersed suspended matter in wastewater can damage expensive equipment that operates on the basis of biological, physical and chemical treatment methods.

2. Theoretical review
To remove from the water such mechanical impurities as sand, iron hydroxide (rust), water clarification filters or, in simple terms, mechanical filters are used. The mechanical filters are a fiberglass housing filled with a filtering load and a control unit that allows to carry out the stages of backwash and washing of the load in an automatic mode.

Physical and chemical; consists in the addition of a special substance – a flocculant or coagulant for the treatment of effluents from organic impurities. As a result of the chemical reaction of this reagent with impurities, colloids, insoluble constituents, and also part of the soluble components are released, eventually the concentration of harmful substances is significantly reduced, soluble compounds become safe, the composition is neutralized, and subsequent remilling becomes more efficient.

Biological method is based on the use of living microorganisms, which as a result of their vital activity lead to the restoration of organic matter and its oxidation, removing from the water the colloids and suspensions that are food for them.

Chemical method consists in neutralization, oxidation and restoration.
Neutralization occurs by the addition of reagents. To neutralize acidic waters, NaOH, KOH, Na₂CO₃, NH₄OH (ammonia water), CaCO₃, MgCO₃, (CaCO₃-MgCO₂), cement can be used. However, the cheapest reagent is calcium hydroxide (lime milk) with active lime content of Ca(OH)₂ 5-10%. Soda and sodium hydroxide should be used if they are waste products. Sometimes, various waste products are used for neutralization. For example, slags of steelmaking, ferrochromium and blast-furnace industries are used to neutralize waters containing sulfuric acid.

The following oxidizing agents are used for wastewater treatment: gaseous and liquefied chlorine, chlorine dioxide, calcium chlorate, calcium and sodium hypochlorites, potassium permanganate, potassium bichromate, hydrogen peroxide, air oxygen, peroxosulfuric acids, ozone, pyrolusite, etc. Such microorganisms are actively used in devices for wastewater treatment from organic impurities.

The analysis of literary data has shown [1-4], that by present time there is no effective and universal method for cleaning storm drains. Existing chemical, mechanical and biological methods in some cases are quite effective in combination with each other, which is connected with high capital investment and operating costs, so it is necessary to use the most effective methods of purifying aqueous wasters, and make every effort to ensure the possibility of reusing the purified process fluid in subsequent production processes.

The most perspective and effective method of purification of natural and waste water is sorption, the advantages of this method are good process control, relative simplicity of the plant design, high reliability and high degree of purification [5-8]. There are no secondary impurities.

At present, plant waste from the agro-industrial complex is a generally available and relatively cheap raw material for the production of sorbents. In particular, there are various ways of modifying the surface of sorbents: enhancing ion-exchange and oxidation-reduction properties, fixing on the surface of heteropolar functional groups, introducing complexing agents into the carbon matrix or, on
the contrary, removing the structure-forming matrix of silicon dioxide from the surface of the carbon sorbent and much more.

3. Practical importance, implementation and results

In work it has been studied the adsorption capacity of the carbon-mineral sorbent obtained from the reed stems of the South in relation to medium and macromolecular organic compounds, as well as to petroleum products, phenols and heavy metals.

The porous carbon-mineral sorbent is obtained from the reed stems of the South (Phragmites australis) by carbonization. For this, the reed stalks were crushed, heated at 450 – 500 °C for 10-15 minutes, until a loss of 70% of the mass. The selected temperature regime avoids the fritting of SiO₂ in the silicate component, which is part of the initial raw material. The formed coal was cooled in water, treated with a 2-5% solution of nitric acid to remove surface mineral impurities from the sorbent (metal ions), washed once in water and dried at 100-150 °C to constant weight. Absence of steam activation of the sorbent, allows to reduce the volume of micropores obtained to 2-10% (pore radius less than 2.5 nm).

The treatment with a 2-5% solution of nitric acid leads to demineralization of near-surface impurities of the carbon-mineral sorbent. At the stage of carbonization of the crushed reed, a carcass containing carbon and silicate constituents is formed. Depending on the type of the initial raw material and the carbonization temperature of the organic component, the content of the silicate component varies in the range of 20-30%. The process is carried out until the obtaining of a sorbent containing 70-80% of the carbon component, 29-19% of the silicate component and 1% of water [9].

Physicochemical properties of the carbon-mineral sorbent from the reed stems of the South are determined according to GOST (Russian Federation) 4453-74, 16190-70, 12597-67, 17219-71, 12596-67, the results are presented in Table 1.

Table 1. Physical and chemical characteristics of carbon-mineral sorbent from the reed stems of the South.

| Diameter of particles (mm) | Porosity to acetone (%) | Moisture content (%) | Adsorption activity by methylene blue (mg/g) | V₅₅ of water pore, (cm³/g) | pH of the aqueous suspension |
|----------------------------|-------------------------|---------------------|---------------------------------------------|---------------------------|-----------------------------|
| 0.01 – 0.5 | 10.00 | 1 | 230 | 25.4 | 0.71 | 6.8 – 7.3 |
| Specific surface (m²/g) | 1021 | Bulkdensity(g/cm³) | 0.218 | Ashcontent (%) | 21.4 |

The carbon-mineral sorbent obtained from the reed stems of the South has a moderately distributed size of macro- and micropores. Table 2 shows the results of an investigation of the adsorption capacity of a sorbent obtained from reed stems of the South towards medium [10-13] and macromolecular organic compounds [14-17].

Table 2. Sorption capacity of carbon-mineral sorbent from the reed stems of the South towards the organic compounds.

| Limit capacity of sorbent (mg/g) | Content in the initial solution (mg/dm³) | Content in solution after sorption (mg/dm³) | Purification efficiency of aqueous solution (%) |
|---------------------------------|----------------------------------------|--------------------------------------------|-----------------------------------------------|
| Phenol                          | 0.000 | 0.000 | -                              | 99.60                                      |
| 14.70                           | 0.040±0.001 | 0.070±0.001 | 99.86                                      | 99.86                                      |
| 75.000                          | 0.100±0.002 | 0.120±0.002 | 99.88                                      | 99.88                                      |
### Petroleum hydrocarbons

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 1.000 | 0.000 | 100     |
|          | 5.000 | 0.000 | 100     |
|          | 10.000| 0.000 | 100     |

**Barbiturates and derivatives of barbituric acid. They are used as hypnotics, sedatives or anticonvulsants.**

| Cyclobarbital-5-Ethyl-5-(cyclohexen-1-yl)-barbituric acid |
|---------------------------------------------------------|
|                                                        |
| 0.000                                                    | 0.000 | -       |
| 1.000                                                    | 0.050±0.001 | 95.00  |
| 5.000                                                    | 0.050±0.001 | 99.00  |

### Triazolam

8-chloro-6 (ortho-chlorophenyl)-1-methyl-1H-S-triazolo [4,3-a] [1,4] benzodiazepine

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 1.000 | 0.060±0.001 | 94.00  |
|          | 7.000 | 0.050±0.001 | 99.30  |

### Doxylamine

2 - [α [2- (dimethylamino)ethoxy]-α-methylbenzylpyridine

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 1.000 | 0.020±0.001 | 98.00  |
|          | 5.000 | 0.050±0.002 | 99.00  |
|          | 10.000| 0.090±0.002 | 99.10  |

**Means for the treatment of infectious diseases. Antibiotics. They are used as antimicrobial, antibacterial drugs.**

### Tetracycline

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 10.000| 0.010±0.001 | 99.90  |
|          | 50.000| 0.050±0.002 | 99.90  |
|          | 100.000| 0.010±0.002 | 99.99  |

### Adriamycin (Doxorubicin)

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 10.000| 0.010±0.001 | 99.90  |
|          | 50.000| 0.050±0.001 | 99.90  |
|          | 100.000| 0.100±0.003 | 99.90  |

**Antiarrhythmic drugs. They are used as local anesthetics and to reduce the excitability of membranes.**

### Procainamide 4-amino-N-[2- (diethylamino) ethyl] benzamide hydrochloride

|          | 0.000 | 0.000 | -       |
|----------|-------|-------|---------|
|          | 1.000 | 0.010±0.001 | 99.00  |
|          | 5.000 | 0.010±0.001 | 99.80  |
|          | 10.000| 0.030±0.001 | 99.70  |

### Amiodarone

[2-butyl-3-benzofuranyl]-[4- (2-diethylaminoethoxy)-3,5-diiodophenyl]-methanone hydrochloride

|          | 0.000 | 0.00 | -       |
|----------|-------|-----|---------|
|          | 1.000 | 0.010±0.001 | 99.00  |
|          | 5.000 | 0.060±0.003 | 98.80  |
|          | 10.000| 0.120±0.003 | 98.80  |
Psychotropic medicines. Neurolethics. They are used as sedatives.

Aminazin-2-chloro-10-(3-dimethylaminopropyl) phenothiazine hydrochloride

| Concentration (mg/L) | 0.000 | 0.000 | 0.010±0.001 | 0.020±0.002 | 0.050±0.002 |
|----------------------|-------|-------|-------------|-------------|-------------|
| 35.00                | 99.00 | 99.60 | 99.60       | 99.50       |             |

Tricyclic antidepressants. Inhibitors of neuronal capture.

Amitriptyline 5- (3-dimethylaminopropylidene)-10,11-dihydrodibenzocycloheptene hydrochloride

| Concentration (mg/L) | 0.000 | 0.000 | 0.020±0.001 | 0.060±0.002 | 0.050±0.007 |
|----------------------|-------|-------|-------------|-------------|-------------|
| 30.00                | 99.60 | 99.40 | 99.90       |             |             |

Tranquilizers. They are used as sedatives, anticonvulsant and psychotropic drugs, with neurotic and neurosis-like disorders.

Phenazepam 7-bromo-5- (ortho-chlorophenyl) -2-3-dihydro-1H-1,4-benzodiazepin-2-on

| Concentration (mg/L) | 0.000 | 0.000 | 0.020±0.001 | 0.090±0.002 | 0.120±0.005 |
|----------------------|-------|-------|-------------|-------------|-------------|
| 20.00                | 98.00 | 99.60 | 99.10       | 99.10       | 99.60       |

Antihistamines. H1-histamine receptor blockers. They are used in the treatment of allergic diseases.

Diprazine

10- (2-dimethylaminopropyl) phenothiazinehydrochloride

| Concentration (mg/L) | 0.000 | 0.000 | 0.010±0.001 | 0.050±0.003 | 0.070±0.003 |
|----------------------|-------|-------|-------------|-------------|-------------|
| 25.00                | 99.00 | 99.00 | 99.30       |             |             |

Adrenocortical hormones and their synthetic analogues. They are used as anti-inflammatory, antiallergic, immunosuppressive drugs.

Hydrocortisone 17-oxy corticosterone

| Concentration (mg/L) | 0.000 | 0.000 | 0.020±0.001 | 0.030±0.001 | 0.030±0.001 |
|----------------------|-------|-------|-------------|-------------|-------------|
| 20.00                | 98.00 | 99.40 | 99.70       |             |             |

Table 3 shows a comparative characteristic of the efficiency of cleaning aqueous media from organic compounds, petroleum products and metal ions by the carbon-mineral sorbent obtained by us and a sorbent obtained from sapropel [18].

**Table 3.** Comparative characteristics of the efficiency of water purification by the proposed sorbent from the reed stems of the South and sorbent obtained from sapropel.

| Sorbent            | Phenol | Petroleum products | Fe$^{3+}$ | Cu$^{2+}$ | Zn$^{2+}$ |
|--------------------|--------|--------------------|----------|----------|----------|
| Comparativesorbent | 73     | 95                 | 93       | 87       | 35       |
| Proposedsorbent    | 99     | 100                | 96       | 94       | 99       |
4. Conclusions
As a result of the work done, it was established that the carbon-mineral sorbent obtained from the reed stems of the South has moderately distributed sizes of macro- and micropores. The presence of two constituents, carbon and silicate, in the structure of the obtained sorbent promotes the sorption of phenols, hydrocarbons, barbiturates, cholesterol derivatives, aminoglycosides, anthracyclines and other compounds, as well as ions of heavy metals, which makes it possible to use sorbent in the chemical industry for purification of sewage, natural waters and be proposed for the purification of biological fluids.

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