PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2024, **58**(2), p. 159–163

COMMUNICATION

Chemistry

STUDY OF SORPTION PROPERTIES OF OXIDIZED SORBENTS OBTAINED FROM DOGWOOD SEEDS

S. B. MKHITARYAN [1*], S. M. VARDAPETYAN [2**], O. A. KAMALYAN [1,3***]

[1] *Armenian National Agrarian University (ANAU), Armenia*
[2] *Chair of Pharmaceutical Chemistry and Pharmacognosy,*
Institute of Pharmacy, YSU, Armenia
[3] *Institute of Chemical Physics after A.B. Nalbandyan NAN of RA, Armenia*

The results of studying the sorption properties of bifunctional carbon sorbents obtained from dogwood seed shells are presented. It is shown that the greatest content of surface oxygen-containing groups is provided by oxidation of carbonizates by hydrogen peroxide generated in an electrochemical cell. The optimal oxidation mode was the use of 5 *M* sulfuric acid solution as an electrolyte, and the current density was 15 mA/cm^2.

The sorption of Fe^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} ions was studied under static conditions at pH 1.5–6.0. It is shown that the highest degree of extraction of these ions is observed at pH 4.5–5.0. The optimal conditions of extraction of the ions, distribution coefficients and static sorption capacities are presented. According to the distribution coefficients, the indicated ions are distributed as follows: $Fe^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > Al^{3+} > Mg^{2+} > Ca^{2+}$.

https://doi.org/10.46991/PYSU:B.2024.58.2.159

Keywords**:** bifunctional sorbents, enterosorption, oxidized coals, sorption of heavy metals.

Introduction. Unfavorable ecological conditions in the environment and, as a result, various diseases that lead to the accumulation of various toxic substances in the organisms of human beings and animals require a new approach in dealing with health security issues. Currently, the most effective way to solve this problem is sorption detoxification of the bodies of animals and people. These include hemosorption, i.e. purification of blood outside the body, plasma sorption, lymphosorption, enterosorption, i.e. detoxification of the body in gastrointestinal tract and others.

The most promising method of detoxification is hemosorption, which is based on the removal of various toxic substances from the body at different diseases – cancer, anti-immune, infectious, allergic and others.

---

[*] E-mail: sevda.mkhitaryan@mail.ru
[**] E-mail: svardapet@ysu.am
[***] E-mail: kamalyan@ysu.am

Depending on the type of connection between the sorbent and sorbtive, hem sorbents conventionally are divided into two groups. The first group includes neutral adsorbents such as activated carbons, silica gels, alumina gels, neutral copolymers without ionic groups. Their sorption properties are due to van der Waals interactions between the adsorbent and adsorbate. Therefore, their sorption capacity is determined basically by their textural parameters – specific surface area, average pore size, specific pore size, fractal dimension of the surface, etc.

To the second group of hemosorbents belong ion exchange sorbents, the sorption properties of which are mainly due to the chemical nature of the surface. From a practical point of view, combined or bifunctional sorbents have broader applications which have the properties of both types of sorbents. The basic method of their preparation is to provide different functional groups at the surface of neutral sorbents by means of chemical modification [1–4].

For medical applications the main focus is on carbon sorbents, as they mostly meet quite strict requirements introduced to medical sorbents. To get such adsorbents, generally cheese of vegetable origin is used, mainly various fruit pits, since they provide not only the highest degree of chemical purity of the sorbents, but also the required reproducibility of the properties of the sorbents. The article presents the results of the study of sorption properties of bifunctional carbon sorbents obtained from the shell of dogwood seels.

Materials and Methods. For carbonization (charring) of pre-washed water, dried at a temperature of 120℃ and crushed (particle size – about 1 *mm*) dogwood seed shells, direct heating was carried out in an electric oven in a rotating quartz reactor in a stream of air or nitrogen (flow rate 0.1–0.5 *L*/*min*) with a programmed heating mode at a rate of 50℃/*h*, in the temperature range of 200–700℃ (Fig. 1). After reaching the required temperature, the samples were removed from the reactor and cooled in a desiccator to room temperature temperatures, weighed and determined by mass loss.

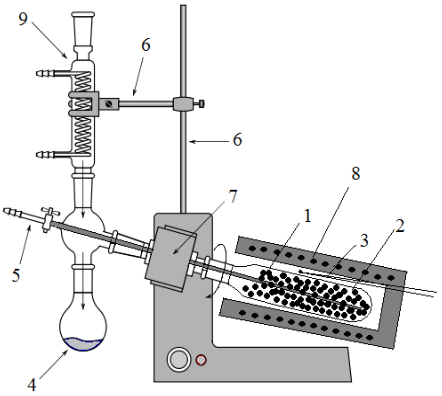


Fig. 1. Scheme of the plant to obtain carbonates:

1) rotating quartz reactor;
2) feedstock;
3) thermocouple;
4) condensate receiver;
5) gas supply valve;
6) tripod;
7) electromotor;
8) heater with thermostat;
9) reflux condenser.

The oxidation of carbonates was carried out at room temperature in an electrochemical cell with intensive mixing with a magnetic stirrer. After drying the samples at 105℃, the content of oxygen-containing surface functional groups on the surface of oxidized carbons was determined by the selective neutralization according to the method described in [5].

Results and Discussion. To obtain carbonizates – products of thermal decomposition of the original plant raw material, a unit with a rotating quartz reactor was used (Fig. 1). This unit allows carbonization to be carried out both in a flow of various gases and in an atmosphere of rarefied air. In addition, it allows heating at a certain speed. Further oxidation of carbonates with various oxidizers made it possible to obtain sorbents with an oxidized surface.

As shown by the corresponding measurements, the largest content of surface oxygenated groups is provided by oxidation of carbonates by hydrogen peroxide generated in an electrochemical cell (Fig. 2). The optimal mode of oxidation is the use of 5 *M* sulfuric acid as an electrolyte solution and density of the current of 15 *mA*/*cm*^{2}.

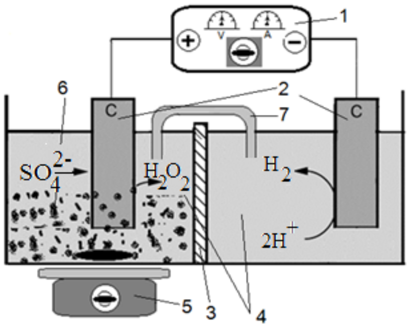
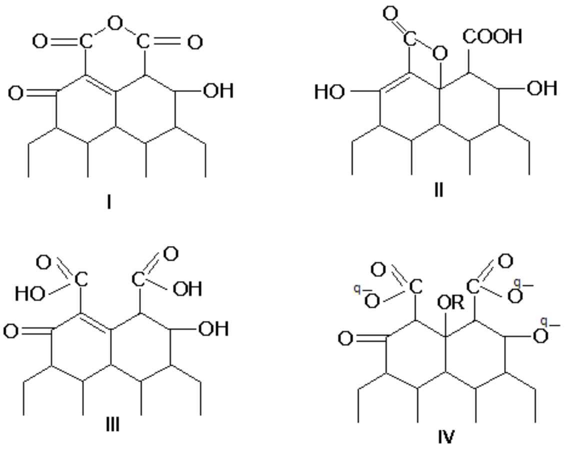


Fig. 2. The scheme of installation of electrochemical oxidation carbonates:

1) power source;
2) graphite electrodes;
3) glass partition;
4) electrolyte;
5) magnetic stirrer;
6) oxidizable carbonate;
7) electrolyte bridge.

To determine the nature of the functional groups on the surface of oxidized sorbents they are usually titrated with the bases of varying strength – $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa [5, 6]. Given that the hydrocarbonate neutralizes the stronger acid sites, these centers carbonate and carboxyl centers, NaOH – as phenolic centers and C_2H_5ONa – all the acid sites on the results of the titration of these agents can be judged on the availability of certain functional centers on the oxidized surface of carbon sorbents.



Scheme of the surface functional groups on the oxidized carbonate.

Scheme shows of such groups that are most frequently detected on the surface of oxidized carbon sorbents.

In case of insufficiency of water it is likely to form a surface of anhydrate groups I (see Scheme). In this group the hydration proceeds to state II, a carboxyl group, a phenolic hydroxyl group and four membered lactone ring which, under certain conditions, for example under the influence of soda may open and regroup into a quinoid structure to form another carboxyl group. III and IV groupings contain typical carboxyl and phenolic acid groups, which are partially ionized.

As a result of studying the sorption of Fe^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} ions under static conditions at pH 1.5–6.0, it was shown that the highest degree of extraction of these ions is observed at pH 4.5–5.0, and according to the distribution coefficients they are distributed as follows: $Fe^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > Al^{3+} > > Mg^{2+} > Ca^{2+}$.

Table shows the main physical and chemical properties of the obtained sorbent. It not only has the largest number of functional groups, but is also characterized by a large specific surface area that is at Aranovich 280 m^2/g.

Basic physical and chemical characteristics of the oxidized sorbents

Property	Value
Bulk density, kg/m^3	420
Aranovich specific surface, m^2/g	280
The specific pore volume of water sorption, cm^3/g	0.35
Mechanical crushing strength, kg/cm^2	34
Ash content, %	1.8 ± 0.2
The average pore diameter, *nm*	20 ± 2
The sorption capacity for iodine, *mg/g*	35 ± 2
The sorption capacity of Methylene Blue, *g/g*	25 ± 2

Conclusion. Thus, it has been shown that the highest content of surface oxygen-containing groups is provided by the oxidation of carbonates with hydrogen peroxide generated in an electrochemical cell. The optimal oxidation mode turned out to be the use of a 5 *M* sulfuric acid solution as an electrolyte, and the current density was 15 mA/cm^2.

As a result of studying the sorption of Fe^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} ions under static conditions at pH 1.5–6.0, it was shown that the highest degree of extraction of these ions is observed at pH 4.5–5.0, and according to the distribution coefficients they are distributed as follows: $Fe^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > > Al^{3+} > Mg^{2+} > Ca^{2+}$.

Received 01.07.2024
Reviewed 15.07.2024
Accepted 24.07.2024

REFERENCES

1. Pyanova L.G. Carbon Sorbents in Medicine and Proteomics. *Chemistry for Sustainable Development* **19** (2011), 107–116.
2. Andrade J.D., Kunitomo K., et al. Coated Adsorbents for Direct Blood Perfusion: Hema/Activated Carbon. *American Society for Artificial Internal Organs* **XVII** (1971), 222–228.

3. Goulding R. *Use of Coated Adsorbent Hemoperfusion in Acute Intoxication. Artificial Kidney, Artificial Liver and Artificial Cells.* New York, London, Plenum press (1978), 135–142.
4. Terman D.S. *Extracorporeal Immunoadsorbens for Extraction of Circulating Immune Reactants. Sorbents and Their Clinical Applications*. New York, London, Academic Press (1980), 469–491.
5. Boehem J.P. Chemical Identification of Surface Groups. *Proc.: Stereochemistry and Mechanisms of Catalytic Reactions.* Moscow, Mir (1968), 186–288 (in Russian).
6. Kamalyan O.A., Sargsyan A.V., Kamalyan T.O. Activated Charcoal from Grape Seeds as the Sorbents for the Purification of Wines. Int. Conf. “Chemistry and Full Processing of Forest Biomass”. Abstracts. Conf., St. Petersburg (2010), 44 (in Russian).

Ս. Բ. ՄԽԻԹԱՐՅԱՆ, Ս. Մ. ՎԱՐԴԱՊԵՏՅԱՆ, Օ. Ա. ՔԱՄԱԼՅԱՆ

ՀՈՆԻ ԿՈՐԻԶՆԵՐԻՑ ՍՏԱՑՎԱԾ ՕՔՍԻԴԱՑՎԱԾ ՍՈՐԲԵՆՏՆԵՐԻ ՍՈՐԲՈՒՄԱՅԻՆ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ

Ներկայացված են հոնի կորիզների կեղևից ստացված բիֆունկցիոնալ ածխային սորբենտների սորբումային հատկությունները: Ցույց է տրված, որ մակերևութային թթվածնավոր ֆունկցիոնալ խմբերի առավելագույն պարունակությունն ապահովվում է էլեկտրաքիմիական բջջում գեներացված ջրածնի պերօքսիդով կարբոնիզատների օքսիդացմամբ: Օքսիդացման օպտիմալ ռեժիմին համապատասխանում է թթվի 5 *M* կոնցենտրացիան և 15 *մԱ*/*սմ*^{2} հոսանքի խտությունը:

Ուսումնասիրվել է ստատիկ պայմաններում Fe^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} իոնների սորբցիան pH 1.5–6.0 պայմաններում: Ցույց է տրվել, որ ջրային լուծույթներից այդ իոնների կորզման առավելագույն աստիճանը դիտվում է pH 4.5–5.0 պայմաններում: Ներկայացված են իոնների կորզման օպտիմալ պայմանները, դրանց բաշխման գործակիցները և ստատիկ սորբումային ունակությունը: Պարզվել է, որ ըստ բաշխման գործակիցների իոնները բաշխվում են հետրյալ կերպ՝ $Fe^{2+} > Cu^{2+} > Ni^{2+} > Sn^{2+} > Al^{3+} > Mg^{2+} > Ca^{2+}$:

С. Б. МХИТАРЯН, С. М. ВАРДАПЕТЯН, О. А. КАМАЛЯН

ИЗУЧЕНИЕ СОРБЦИОННЫХ СВОЙСТВ ОКИСЛЕННЫХ СОРБЕНТОВ, ПОЛУЧЕННЫХ ИЗ КОСТОЧЕК КИЗИЛА

Приведены результаты изучения сорбционных свойств бифункциональных углеродных сорбентов, полученных из косточек кизила. Показано, что наибольшее содержание поверхностных кислородсодержащих групп обеспечивается окислением карбонизатов пероксидом водорода, генерированного в электрохимической ячейке. Оптимальному режиму окисления соответствуют концентрация 5 *M* раствора серной кислоты и плотность тока 15 *мА*/*см*^{2}.

Изучена сорбция ионов Fe^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Al^{3+}, Mg^{2+}, Ca^{2+} в статических условиях при pH 1.5–6.0. Показано, что наибольшая степень извлечения этих ионов наблюдается при pH 4.5–5.0. Представлены оптимальные условия извлечения ионов, коэффициенты распределения и статические сорбционные емкости. Показано, что по коэффициентам распределения они находятся в следующей зависимости: $Fe^{2+}>Cu^{2+}>Ni^{2+}>Sn^{2+}>Al^{3+}>Mg^{2+}>Ca^{2+}$.