UDC 539.211 : 544.723+54.31

BORONIC-ACID FUNCTIONALIZED MAGNETITE NANOCOMPOSITES FOR FRUCTOSE SENSING

Ye.V. Pylypchuk[1*], Yu.O. Zubchuk[1], P.P. Gorbyk[1]
K.O. Doroshenko[2*], N.G. Antoniuk[2]
[1] O.O. Chuiko Institute of Surface Chemistry, 17, General Naumov Street, Kyiv, 03164, Ukraine
**e-mail: ievgenpylypchuk@gmail.com*
[2] National University of Kyiv-Mohyla Academy, 2, Skovorody Street, 04655, Kyiv, Ukraine
**e-mail: ekaterinka.doroshenko@mail.com*

Abstract.*Method for boronic acid immobilization on the magnetite surface reported.Immobilization of boronic acid on the nanocomposite surface was confirmed using Fourier-Transform infrared spectroscopy. Proof of principle experiments using obtained nanocomposites showed possibility of their potential application for fructose sensing.*

Keywords: *multifunctional nanocomposites, absorption of fructose,magnetite, Alizarin Red S, boronic acid.*

Introduction. Recognition of different simple sugars in human blood is an important taskforcurrent medicine. The most promising way to construct fructose-sensitive materials is to use the ability of boronic acid to form reversible covalent complexes with 1,2- and 1,3-diols [1-2]. Boronic acids has relatively small toxicity and can be considered as “green” compounds [3].

Magnetite, Fe_3O_4 is natural mineral with high biocompatibitily [4]. Sensor applications in combination with magnetic properties of boronic acid-containing Fe_3O_4 nanocomposites allow us to create highly biocompatible multifunctional “green” materials for fructose detection.

Experimental. Magnetite was modified by 3-APTES using standart method [5]. 5-Formil-2-furyl boronic acid (furyl borate) was immobizlied on the surface of Magnetite/3-APTES composite in ethanolic solution. Immobilization of Alizarine Red S was performed in phosphate buffer (pH=7.4).

Results and discussion. The general scheme of Fe_3O_4/3-APTES/boronic acidnanocomposite synthesis is shown in Fig. 1. In the IR spectra of the obtained composite and initial furyl borate (Fig. 2) characteristic absorption bands are observed. They can be attributed to formilgroupinfuryl borate (1735 and 1803 cm^{-1}, probably splitting is due to intramolecular interactions of formil residuewith hydroxyl groups of boronic acid).After interaction withaminomagnetite, absorption bands of formil disappear, what may indicate the formation of Fe_3O_4/3-APTES/boronic acidcomposite. Absorption bandsof –B–C bondare is observed at 900 cm^{-1}, absorption bandsof –B– O bond is observed at 1350 cm^{-1}.

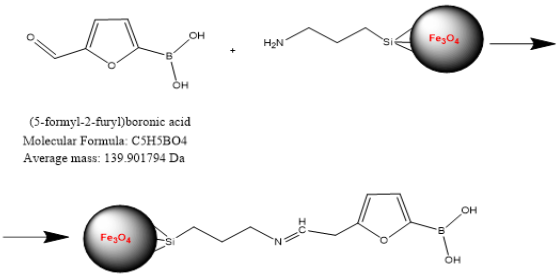


Fig. 1. *Scheme of synthesis of Fe_3O_4/3-APTES/Boronic Acid Nanocomposite*

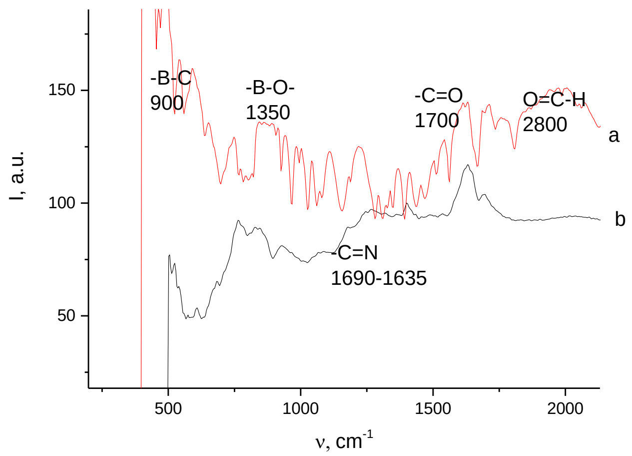


Fig. 2. *IR spectra of furfurylborate (a) and nanocomposite Fe_3O_4/3-APTES/boronic acid (b).*

Based on the data obtained by IR spectroscopy furylborate was successfully immobilized on the surface of magnetite.

*The study of competitive interaction and nanocompositeFe_3O_4 / 3-ARS / furfurylborate with Alizaryn Red S and Fructose***.** The method is based on the ability of immobilized boronic acid to bind cis-diol form of hydrocarbons specificly(Fig. 3) [6].

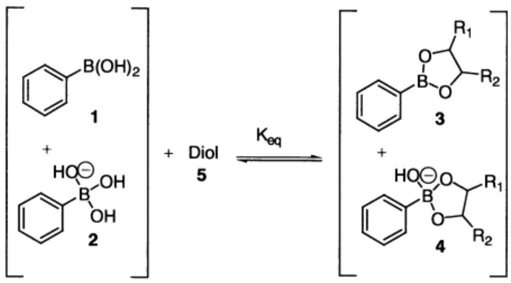
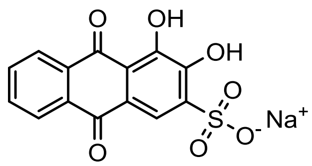


Fig. 3. *The binding of cis-diol with boronic acid [7].*

AlizarinRed S (ARS) in phosphate buffer (pH = 7.4) is used as an indicator in these types of reactions, λ_{max} = 423 nm.



Molecular Weight 342.26

According to the literature, a competitive reaction between sugar and ARSh occurs in the processof absorption of sugars on the surface of the material which contain acidic surface groups with Boron (Fig. 4):

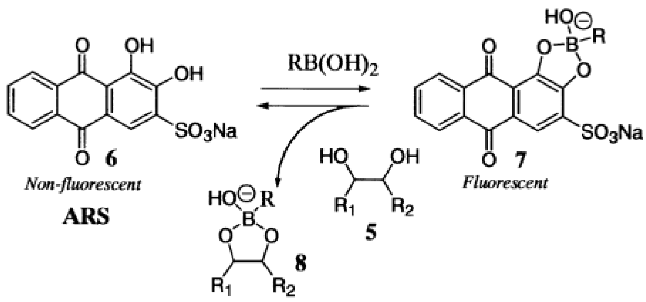


Fig. 4. *The competitive reaction between sugars and ARS.*

Thus, there is a "switch" of ARS molecules from non-fluorescence condition to fluorescence one. Thus, the content of cis-diols in solution can be quantitatively evaluated with the fluorescence of obtained conjugate. In addition, there is a shift of the maximum of absorption band of cis-diol derivate in the visible range. In our work itis demonstrated with the formyl-furylboric acid and ARS in phosphate buffer (Fig. 5).

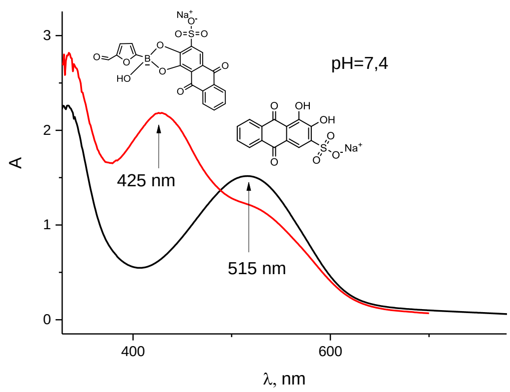


Fig. 5. *The absorption spectrum of ARS in phosphate buffer (1) and its conjugate acid with formyl-furfurylboric acid.*

Scheme of ARS binding with the surface of Fe_3O_4/3-APTES/boronic acid nanocomposite is showen in Fig. 6.

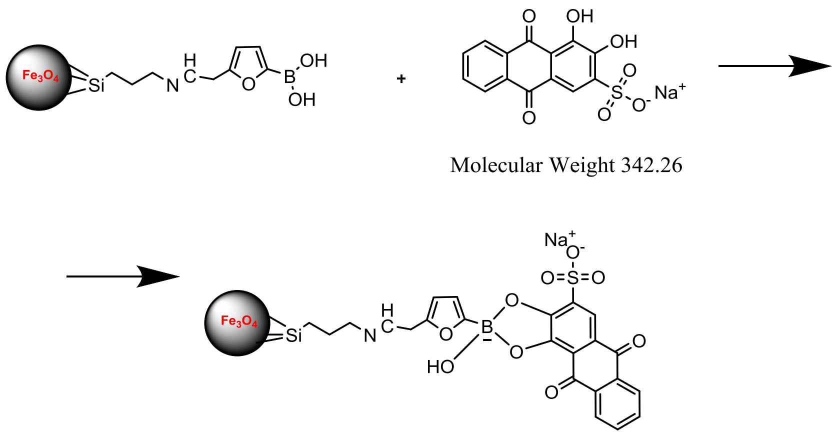


Fig. 6. *Scheme of ARS binding with the surface of Fe_3O_4/3-APTES/boronic acid nanocomposite*

Based on literature data, in case of the addition of carbohydrate in the form of cis-diol form the competitive replacement ARS on the surface of the composite to sugar molecules should occur.

Release of ARS when fructose is added was confirmed by photocolorimetric method. A model experiment was being conducted that based on competitive sorption phenomena between ARS at the surface of nanocomposites and fructose. It passes according to this scheme (Fig. 7).

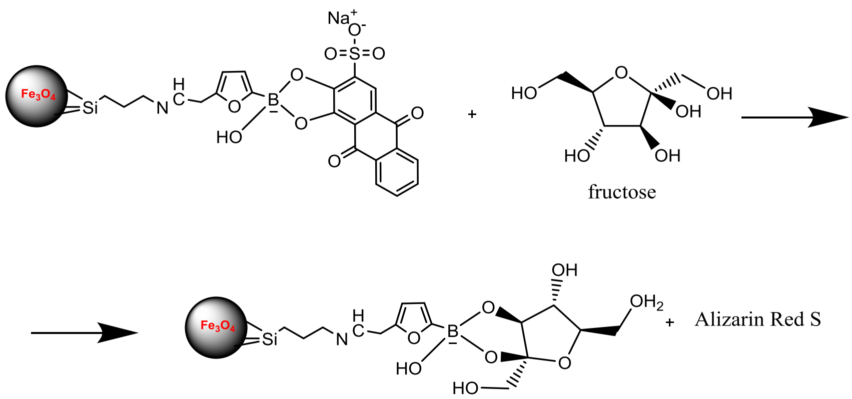


Fig. 7. *Competition between ARS and fructose.*

Conclusions. Modification of Fe_3O_4 by boronic acid could be realized throughout imine bond formation using formil-furyl boronic acid and NH_2-containing magnetite. Obtained Fe_3O_4/3-APTES/boronic acidcomposite show characteric adsorption band in FTIR spectra and able to interact with 1,2-diols (e.g. ARS). Preliminary experiments confirmed possibility to detect glucose using Fe_3O_4/3-APTES/boronic acid/Alizarin Red S nanocomposites according to competitive interaction in phosphfte buffer.

Acknowledgements. This research was supported by project N 38-16 *“Synthesis and properties of novel supramolecular nanostructures and*

composites, absorbing microwave electromagnetic and neutron radiation” in framework of NAS of Ukraine comprehensive program of basic research "Fundamental problems of new nanomaterials and nanotechnologies".

References

1. *Cambre J. N., Sumerlin B. S.* Biomedical applications of boronic acid polymers // Polymer. 2011. V. 52. P. 4631-4643.
2. *Salazar-Mendoza D., Cruz-Huerta J., Höpfl H., Hernández-Ahuactzi I. F., Sanchez M.* Macrocycles and Coordination Polymers Derived from Self-Complementary Tectons Based on N-Containing Boronic Acids // Crystal Growth and Design. 2013. V. 13. P. 2441-2454.
3. *Savsunenko O., Matondo H., Frencechi-Messant S., Perez E., Popov A., Rico-Lattes I., Lattes A., Kaprichev Ye.* Functionalized vesicles based on amphiphilic boronic acids: a system for recognizing biologically important polyols // Langmuir. 2013.V. 29. P. 3207-3213.
4. *Kołodyńska D., Gęca M., Hubicki Z.* Development of New Effective Sorbents Based on Nanomagnetite // Nano Res. lett. 2016. V. 11.1. P. 1-10.
5. *Pylypchuk Ye., Zubchuk Yu., Petranovska A., Turanska S., Gorbyk P.* Syntesis and properties of Fe_3O_4/hydroxyapatite/pamidrinic acid/DTPA/Gd^{3+} // Him. Fiz. Techn. Pov. 2015. V. 3. P. 326-335.
6. *Emanuel V., Karyagin Y., Emanuel U.* Comparison of methods for determining of glycolysised hemoglobin // Lab. Medicine. 2002. V. 5. P. 98-104.
7. *Springsteen G., Wang B.* A detailed examination of boronic acid–diol complexation // Tetrahedron. 2002. V. 58. P. 5291–5300.

УДК 539.211 : 544.723+54.31

НАНОКОМПОЗИТИ НА ОСНОВІ МАГНЕТИТУ ФУНКЦІОНАЛІЗОВАНОГО БОРНОЮ КИСЛОТОЮ ДЛЯ ВИЗНАЧЕННЯ ФРУКТОЗИ.

Є. В. Пилипчук[1*], Ю. О. Зубчук[1], П. П. Горбик[1]
К. О. Дорошенко[2*], Н. Г. Антонюк[2]

[1]Інститут хімії поверхні ім. О.О. Чуйка, вул. Генерала Наумова17, 03164,Київ, Україна,
**e-mail: ievgenpylypchuk@gmail.com*

[2]Національний університет «Києво-Могилянська академія», вул.Г. Сковороди 2, 04655, Київ, Україна.
**e-mail: ekaternka.doroshenko@gmail.com*

Резюме. *Висвітлено метод іммобілізації фурфурилборної кислоти на поверхню магнетиту. Іммобілізацію на поверхні нанокомпозиту підтверджено за допомогою ІЧ спектроскопії з Фур’є-перетворенням. Контрольно-перевірочний експеримент отриманого нанокомпозиту показав потенційну можливість застосування його для визначення фруктози.*

Ключові слова: *поліфункціональні нанокомпозити, абсорбція фруктози, магнетит, алізарин червоний S, борна килота.*