

SORPTION PURIFICATION OF WATER FROM HEAVY METAL IONS USING SULFOUGL

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Abstract: *Introduction.* The sorption capacity of modified carbon has been investigated; the possibility of creating a sorbent for iron (II, III) in water bodies with a purified water yield of up to 0.01 mg/l has been shown. The purpose of the work. To create a new cheap sorbent based on sulfougl, to study its sorption characteristics by the method of solid-phase photometric determination of Fe (II, III) with a low detection limit. *Methodology.* The sorption capacity with respect to iron ions (II, III) modified with sulfougl has been studied. The sulfogroup used as a modifier has been used in the photometric determination of Fe (II, III) and has been used in the analysis of waters for the total iron content. *Results and discussion.* Today, thousands of sorbents are produced with various matrix materials, functional groupings, methods of their fixation, containers, mechanical properties, grain and other characteristics. The choice of the optimal sorbent depends on the task assigned to the researcher. *Conclusion.* When choosing a sorbent, it is necessary to take into account the concentration mode. Thus, after the sorption extraction under the static conditions, the sorbent concentrate should be easily separated from the mother liquor; when used in the dynamic mode, it is undesirable to use strongly swelling sorbents, as well as too small fractions of sorbents. The development of simple methods of water purification from heavy metals, in particular, from the widespread iron (II, III) cation in natural and drinking waters is an important task of analytical chemistry.

Key words: sorption, adsorption, sorbent, complexing, modification

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1. Introduction

Sorption methods are based on complexing reactions on the solid phase of metal ions with a reagent [1, 2]; the well-known, well-proven sorbents based on coal are usually used for their implementation [3]. The known modifications of coal sorbents are presented in [4]. Currently, modified coal (sulfougl) ave been specially developed due to their possible subsequent use in small-sized household filters for the sorption water purification. Sulfougl is porous adsorbents, and is used in several industrial processes. These carbons have often been used to adsorb pollutants present in the gas or liquid phases in order to control environmental pollution, remove organic compounds, or remove toxic metal particles [5]. The whole variety of the obtained carbon sorbents can be classified according to various criteria: the nature of the feedstock (solid, liquid, gaseous), production methods, structural and textural (porosity, surface, pore size and distribution) characteristics and applications. For industries such as leather, textile, metalworking, battery, pigment and metallurgy, toxic metal ions are widely used, which can have an impact on the environment. Moreover, toxic metal ions can accumulate in microorganisms, flora and aquatic fauna, thereby introducing these metals into the food chain and increasing the risk of health problems in humans [6]. The removal of metal ions can be achieved using various techniques, including precipitation, adsorption, ion exchange, membrane processes, electrodialysis and reverse osmosis [7]. Among them, sulfocarbon adsorption is a very effective method due to the large available surface area and the characteristics of modified coal. In addition, modified coal can be obtained from several natural carbonaceous materials at a relatively low cost [8].

2. The experimental part

The initial solutions, containing iron (ii), iron (iii) 0.1 mg/ml were prepared by dissolving precise attachments of Mora salt (bda.) and iron-ammonium alum (ch.d.a.), respectively, in sulfuric acid solutions. The solutions with lower concentrations were obtained by dilution on the day of using. For the preparation of buffer solutions, ammonium acetate, acetic acid (all h.d.a.) were used [9]. Modified coal was obtained by the method, described earlier [10].

The sorption of iron ions with sulfocarbon was studied in a static mode. To do this, the studied solutions and modified coal plates were placed in vessels with lapped stoppers. Then the vessels were shaken on an electromechanical vibration mixer until sorption equilibrium was established. The sorption value (a , mg/g) was calculated by the formula:

$$a = \frac{(C_0 - [C]) \cdot V}{m},$$

where C_0 - the concentration of the detected compound in the aqueous solution before sorption (mg/ml), $[C]$ - the concentration in the solution after

sorption (mg/ml), V - the volume of the analyzed solution (ml), m - the mass of activated carbon (g).

The equilibrium concentration of iron ions was determined photometrically according to GOST [11]. The determination of the sulfogroup was carried out using a developed photometric technique, based on the absorption of the dipyriddy complex of iron (II). The Baer's law is fulfilled with an excess of iron (II) metal ion under the conditions of complete ligand binding into the complex ($\lambda=540$ nm, $C_{Fe^{2+}} = 0.1$ mg/ml, $C_{dip} = 0.016 \div 0.16$ mg/ml, pH=4).

The optical density of the solutions was measured, using a photo colorimeter.

3. Results and their discussion

To obtain information about the nature of the interaction between coal and sulfuric acid, an isotherm (figure 1) and the kinetic reaction curve (figure 2) of the sulfogroups from an aqueous solution have been obtained. The sorption isotherms have two ascending sections and a plateau between them. The first growth site on the isotherms corresponds to the ionic coordination of the sulfogroup, and the second to the formation of a covalent bond between the sulfogroup and the coal surface [12]. It can be seen from the kinetic migration curve of the sulfogroup that structural changes occur in the first few minutes, as evidenced by the extremum in this area. This is due to the incorporation of the reagent into the matrix and the formation of a new structure [13]. The samples of natural coal after immobilization of the sulfogroup retain their sorption capacity.

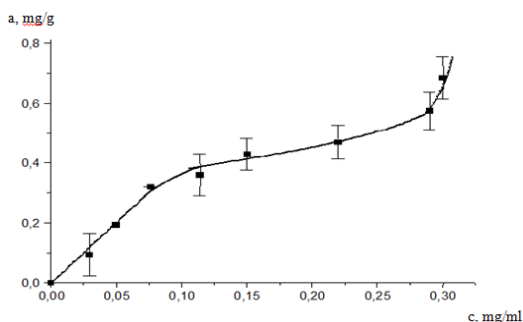


Figure 1 – Isotherm of migration of the sulfogroups to the coal surface ($opm=0.6$ g, $V=30$ ml).

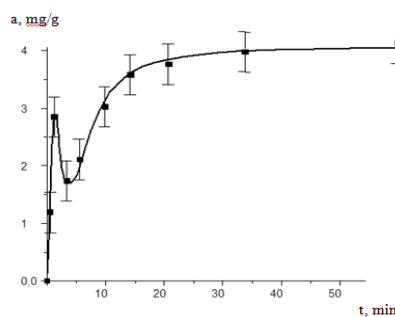


Figure 2 – Kinetic curve of the formation of the covalent bonds of a sulfogroup on the surface.

The sorption properties of sulfougl with respect to iron ions (II, III) have also been presented in the form of a kinetic curve (figure 3).

The kinetic curve of the sorption of iron ions by the modified sulfougl has a classical appearance, which indicates the absence of structural changes in the process of iron extraction (II, III). Probably, the main interactions observed during the sorption are due to the formation of bonds between iron ions and

oxygen of the sulfogroup. The time to establish equilibrium with a volume of 50 ml of test water is approximately 10 min.

The quantitative extraction has been achieved at the concentrations from 0.5 mmol/g at a pH of 6.0-7.0 and with an increase in the surface concentration to 4 mmol/g, little changes, which is due to the ratio of the number of the surface sulfogroups and the content of cations in water (figure 4).

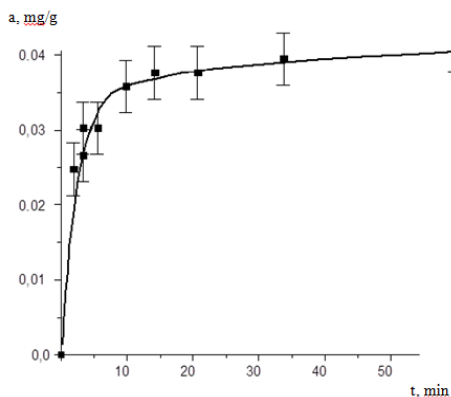


Figure 3 – Kinetic curve of iron (II, III) sorption by sulfocarbon.

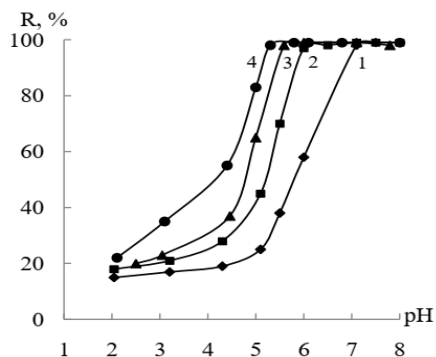


Figure 4 – Dependences of the degree of extraction of Fe(II,III) on pH at the surface concentration of the sulfogroups, mmol/g: 0.1 (1); 0.5 (2); 1 (3); 4 (4).

At the surface concentration of the sulfogroups of at least 0.1 mmol/g, the sorbent quantitatively extracts iron in the pH range of 5.5 – 8.0, which corresponds to the acidity of most surface waters of Kazakhstan. Under optimal concentration conditions, the distribution coefficient is $5 \cdot 10^3 - 1 \cdot 10^4 \text{ cm}^3/\text{g}$.

With an increase in the concentration of surface groups, the pH range of quantitative iron extraction (II, III) shifts to the acidic region due to the intrinsic acidity of the sulfogroups. The confirmation of iron sorption (II, III) due to the interaction with the surface sulfogroups, the minimum sorption value is less than 10% in the entire studied pH range on the unmodified coal. A significant sorption is observed at pH greater than 9, which corresponds to the formation of iron hydroxocomplexes and their deposition on the developed surface of the unmodified coal.

The range of concentrations of iron (II, III) 20 – 500 mg/l has been chosen so as to cover the concentrations in the natural surface waters of Kazakhstan. It has been found that with the help of the proposed matrix, iron (II, III) sorption is possible with a decrease in its concentration to 0.01 mg/l (the sample volume 50 ml), which is 1/30 MPC for drinking water (0.3 mg/l) [14]. The technique has been tested in the analysis of mineral water from a natural source. The results of the determination of iron (II, III) ions by photometric method with 1,10 - phenanthroline in mineral water are presented in Table 1, and indicates the

correctness of the obtained results and the possibility of using modified sulfocarbon for the sorption purification of water from iron (II, III) ions.

Table 1- Results of the determination of iron ions (II, III) (n=3, P=0.95)

Test	Iron content, mg/l		Found by photometric method after sorption, mg/ml	
	Before sorption	S_r	Fe (II, III)	S_r
Mineral spring water	70±5	0.03	0.04±0.01	0.10
Lake water	8±3	0.15	0.07±0.02	0.12
Swamp water	52±3	0.02	0.05±0.02	0.16

The results of the study have shown a possibility of the sorption concentration of iron ions from an aqueous solution in the form of a complex with the sulfogroups on the surface of activated carbon. It has been shown that semi-quantitative determination of iron ions is possible, the relative standard deviation in the region of small iron contents (II, III) does not exceed 0.16.

The most important indicators of the feasibility of using sorbents for analytical purposes are the quantitative extraction of elements, the speed of establishing sorption equilibrium when they come into contact with a metal solution, as well as the ease of its subsequent desorption. The pH range of quantitative extraction ($\geq 99\%$) in static mode is for Fe (III) – pH 3.0–8.5. The sorbed iron cations in the static mode are quantitatively desorbed with 1 M nitric acid solution.

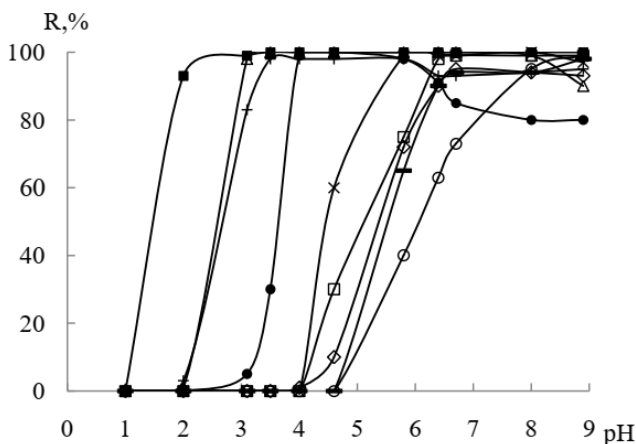


Figure 5 – The degree of extraction of iron ions from the surface of the sorbent into the solution depending from the pH.

4. Conclusion

The obtained results will serve as the basis for the creation of a sorption system for the adsorption of heavy metals from water of natural and technical origin, including chemical enterprises, pharmaceutical, metallurgical,

underground parking, as well as for the treatment of waste waters of chemical, pharmaceutical and other enterprises. Since there is no sorption of iron ions at $\text{pH} < 1.0$, therefore diluted 0.1–2M solutions of nitric acid have been considered as desorbing solutions. The quantitative desorption of Fe (III) in the static mode does not depend on the nature of the acid and is achieved by using 10 ml of 1M HNO_3 . The sorption-desorption cycles of iron ions have been carried out to determine the sorption properties of the synthesized modified coal. The sorbent retains its sorption properties for at least 5 sorption-desorption cycles.

Conflict of Interests: No conflict of interest.

СУЛЬФОКӨМІР КӨМЕГІМЕН АУЫР МЕТАЛЛ ИОНДАРЫНАН СУДЫ СОРБЦИЯЛЫҚ ТАЗАРТУ

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Түйіндеме. *Кіріспе.* Модификацияланған көмірдің сорбциялық қабілеті зерттелді; тазартылған судың шығымы 0,01 мг/л дейін болатын су объектілерінде темірге (II, III) сорбциялық тазалау көрсетілген. *Жұмыстың мақсаты.* Жаңа экономикалық тиімді табиғи залалсыз, қол жетімді сорбент жасау, және оның сорбциялық қабілеттілігінің анықтау шегі Fe (II, III) қатты фазалы фотометриялық анықтау әдісімен зерттеу. *Әдістеме.* Жұмыста модифицирленген көмір (сульфокөмір) темір (II, III) иондарына қатысты сорбциялық қабілеттілік бойынша зерттеулер жүргізілді. Модификатор ретінде сульфокөмірмен Fe (II, III) ионын фотометриялық анықтауда қолданылады және суды жалпы темір құрамына талдау кезінде қолданылады. *Нәтижелер және талқылау.* Бүгінгі таңда әртүрлі матрицалық материалдары, функционалды топтамалары, оларды бекіту әдістері, контейнерлері, механикалық қасиеттері, дәндері және басқа сипаттамалары бар мыңдаған сорбенттер шығарылады. Оңтайлы сорбентті таңдау зерттеушінің алдына қойылған міндетке байланысты. Сорбентті таңдау көбінесе микрокомпоненттің табиғатымен анықталады – бұл компоненттің ерітіндіде болу формасы, ионның немесе молекуланың мөлшері мен заряды, бұл форманың функционалды топтармен немесе тікелей сорбенттің бетімен әрекеттесу қабілеті. *Тұжырым.* Сорбентті таңдағанда концентрация режимін ескеру қажет. Сонымен, статикалық жағдайда сорбциялық экстракциядан кейін сорбент концентраты ерітіндіден оңай бөлінуі керек; динамикалық режимде қолданған кезде қатты ісінетін сорбенттерді, сондай-ақ тым кішкентай сорбент фракцияларын қолдану қажет емес. Бірінші қадам концентрация, ал екінші қадам тазартылған судың сапасын бақылау спектrophотометрия, атомдық абсорбциялық спектроскопия (ААС), индуктивті байланысқан плазмалық атомдық эмиссиялық спектроскопия (АЭС-ИСП), индуктивті байланысқан плазмалық масспектрометрия (МС-ИСП) сияқты спектроскопиялық әдістер болуы мүмкін аралас әдістерде жылдам және жоғары жылдамдықты қолдану мүмкіндігі ескеріледі. Суды ауыр металдардан, атап айтқанда табиғи және ауыз сулардағы жалпы темір (II, III) катионынан тазартудың жедел және қарапайым әдістерін жасау аналитикалық химияның маңызды міндеті болып отыр.

Түйінді сөздер: сорбция, адсорбция, сорбент, комплекс түзуші, модификация

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СОРБЦИОННАЯ ОЧИСТКА ВОДЫ ОТ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ С ПОМОЩЬЮ СУЛЬФОУГЛЯ

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Резюме. *Введение.* Исследована сорбционная способность модифицированного угля; показана возможность создания сорбента для железа (II, III) в водных объектах с выходом очищенной воды до 0,01 мг/л. *Цель работы.* Создать новый дешевый сорбент на основе модифицированного угля (сульфоуголь), изучить его сорбционные характеристики методом твердофазного фотометрического определения Fe (II, III) с низким пределом обнаружения. *Методология.* В работе проведены исследования сорбционной способности по отношению к ионам железа (II, III) модифицированным углем. Используемый в качестве модификатора сульфогруппа используется при фотометрическом определении Fe (II, III) и применяется при анализе вод на общее содержание железа. *Результаты и обсуждение.* На сегодняшний день выпускают тысячи сорбентов с различными материалами матриц, функциональными группировками, способами их закрепления, емкостями, механическими свойствами. Выбор оптимального сорбента зависит от задачи, поставленной перед исследователем. В немалой степени выбор сорбента определяется природой микрокомпонента – формой существования этого компонента в растворе, размером и зарядом иона или молекулы, способностью этой формы вступать в реакции с функциональными группами или непосредственно с поверхностью сорбента. *Заключение:* Так, после сорбционного извлечения в статических условиях сорбент-концентрат должен легко отделяться от маточного раствора; при использовании в динамическом режиме – нежелательно использовать сильно набухающие сорбенты, а также слишком мелкие фракции сорбентов. В комбинированных методиках, где первым шагом является концентрирование, а вторым контроль качества очищенной воды могут выступать спектроскопические методы, такие как спектрофотометрия, атомно-абсорбционная спектроскопия (ААС), атомно эмиссионная спектроскопия с индуктивно связанной плазмой (АЭС-ИСП), масс-спектрометрия с индуктивно связанной плазмой (МС-ИСП), учитывается возможность быстрого и количественного элюирования элементов. Разработка экспрессных и простых методов очистки воды от тяжелых металлов, в частности, от распространенного катиона железа (II, III) в природных и питьевых водах является важной задачей аналитической химии.

Ключевые слова: сорбция, адсорбция, сорбент, комплексообразующие, модификация

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