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# INVESTIGATION OF THE PHYSICO-CHEMICAL PROPERTIES OF PHOSPHORUS-CONTAINING POLYMER SORBENT ON THE BASE OF POLYBUTADIENE

**R.M.ALOSMANOV, A.A.AZIZOV, K.N.ORUJOVA,**
**I.A. BUNYAD-ZADEH, A.M.MAHARRAMOV**
***Baku State University***
***r_alosmanov@rambler.ru***

*In the present work the acid-base properties of phosphorus-containing polymeric sorbent on the basis of polybutadiene have been investigated using the method of pothentiometric titration and sorption properties in relation to copper ions have been studied. It has been revealed that the investigated sorbent has polyfunctional nature and for every type of functional groups the* $pK_{ion}$ *values have been calculated. It has been established that maximum copper ions sorption is observed at pH=6. Sorption isotherm, processed by Langmuir and Freundlich models allows us to conclude that the copper ions sorption occurs on energetically homogenous functional groups with the formation of monomolecular layer of sorbate.*

Heavy metals are permanent chemical contaminants of cumulative action with specific toxic properties. During processing ores, incineration of energy carriers, use of heavy metals, their huge quantities occur in the atmosphere and reservoirs as waste products. Getting into an aquous medium they interact with other components generating hydrated ions, oxyhydrates, ion couples, inorganic and organic complex compounds. The accumulation of heavy metals in the wildlife causes serious anxiety all over the world and stimulates search and development of the most effective ways of the solution for this problem, one of which is their removal by using polymeric sorbents [1].

For this purpose phosphorus-containing sorbents (PhCS) have wide opportunities, which allow them to carry out extraction of heavy metals from aquous mediums[2-4] effectively. Their main physico-chemical properties, i.e. acid-base and sorption, are determined by the nature of polymeric matrix and functional groups. At present, detailed information [2-4] on research of these properties for different phosphorus-containing sorbents in the industrial scale and also synthesized in laboratory conditions has been presented in references. Taking into consideration the fact that the pointed properties are determined mainly by the choice of initial components, by means and conditions of synthesis procedure, the study of corresponding properties for each new synthesized sorbent is considered necessary.

In the current work the results of the investigation on the study of acid-base and sorption properties of PhCS obtained on the basis of polybutadiene are presented.

## Experimental

PhCS has been obtained by means of oxidative chlorphosphorylation of polybutadiene under the influence of $PCl_3$, in the presence of oxygen and further hydrolysis of the obtained modificate [5]. The obtained sorbent has been purified by the known procedure [6] and dried at 323 K in the vacuum oven.

Salts, acids and the bases of classification (chemically pure or pure for analysis grade) have been used without additional purification.

The metal solution has been prepared by dissolving the weighed corresponding salt of $CuSO_4 \cdot 5H_2O$ in distilled water. The necessary acidity of the solution (pH=3-9) has been created by means of acetate-ammonia buffers. For pH1 and pH2 preparation the 0.1N HCI solution has been used. The components of the buffer solutions (HCI, $CH_3COOH$, $NH_3$) were of chemical or analytical reagent grade. The pH values have been controlled by means of pH-meter "Mettler Toledo".

To determine the ionization constants ($K_{ion}$) it was necessary to define in advance the static sorption capacity of sorbents ($SSC_{Na+}$) on Na-ion, which are specified by the features of the investigated sorbent [6], unlike the methods applied to soluble reagents [7].

To determine $SSC_{Na+}$, 1.00g of sorbent in H form has been placed into waterproof flasks; 200 ml of 0.1M NaOH has been added into each of them and mixed by nitrogen current. For each of the sorbent three parallel tests have been prepared. Then the flasks have been closed with the covers (caps) and placed into exsiccator where they have been kept for 24 hours at 293 K, periodically shaking the mixture. On reaching equilibrium of protons substitution in functional groups for Na-cations, the stock solution above the sorbent has been taken and titrated with 0.1M HCI in the presence of a few drops of indicator- 0.1% water solution of red kresol [6].

The value of $SSC_{Na+}$ (mmol/g) has been calculated by equation:

$$SSC_{Na+} = \frac{(200K - 200/25 \cdot V_1 \cdot K_1) \cdot 0.004 \cdot 1000}{40g} = \frac{200K - 8V_1K_1}{10g} \qquad (1)$$

where V is the volume of HCI, used while titrating, ml; K-correlation coefficient on 0.1M NaOH normality; $K_1$ - correlation coefficient on 0.1M HCl; 0.004-titre of 0.1M NaOH; 40-molecular weight of NaOH ; g – sorbent mass, g

Ionization constants of PhCS have been calculated on the basis of the data of potentiometric titration using the method of separate weighing [6]. Sorbent samples of 0.1g in H-form have been placed in bottles of 35 ml by volume and for reaching the constant ion-force values ($\mu$=1) 15 ml of 1M NaCI has been added. An hour later 10ml of 1M NaCI and different quantities of 0.1 M NaCI were added to each of the bottle. The necessary quantity of NaOH was determined so that the value of full neutralization degree of functional groups (Q) changed in a range of 0 up to $SSC_{Na+}$. The solutions were stirred by nitrogen current and kept in the nitrogen-filled exsiccator at ambient temperature (293K) for 24 h in order to reach the ionic equilibrium and then pH of the solution has been measured.

Sorption of metal ions has been studied in the static mode. The weighed samples of sorbent (0.5 g) have been placed into a number of test-tubes and filled up with solutions of suitable electrolytes of 1 mmol/dm$^3$ concentration and 0.15 dm$^3$ volume and set point of pH, and had been kept until the equilibrium in the system was obtained at 293 K. The previously determined equilibrium time was ~ 240 min. After the time, the solution has been filtrated. The concentration of metal ions in the filtrate has been determined, the quantity of sorbed metal on a gram of the sorbent and sorption degree (R, %) have been calculated by equation (2) and (3)

$$C_a = (C_0 - C_e) \cdot V_2 \quad (2)$$

$$R = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (3)$$

where $C_a$ - the quantity of sorbed metal on a gram of the sorbent, $C_0$, $C_e$ - initial and equilibrium concentration of metals ions in solution, respectively, mmol/dm$^3$, $V_2$ – solution volume, corresponding to one gram of the sorbent, dm$^3$

## Results and discussion

On the basis of potentiometric titration data, the integral curve in "pH-Q" coordinates has been plotted, where Q is titrant amount (mmol/g), and by graphical differentiation of integral curve the graphical curve in "ΔpH/ΔQ-Q" coordinates has been obtained (fig.1).

As seen from fig.1, the integral curve has a stepwise form, but the differential curve has two picks, and that testifies polyfunctionality of the studied sorbent, containing functional groups of various nature.

The ionization constants of functional groups have been calculated according to the potentiometric titration data. For each point of titration the neutralization degree of functional-analytical groups by 0.1M NaOH (mmol/g) standard solution has been calculated. The calculation of α value for each ionization step has been done as ratio of added 0.1M NaOH (mmol) matter quantity to total matter amount (mmol) for each active group in 0.100g of sorbent by equation:

$$\alpha = \frac{N \cdot V_3}{g \cdot SSC} \quad (4)$$

where N- molarity of NaOH solution, V-volume of added 0.1M NaOH (ml), g-weight of sorbent (g), SSC-static sorption capacity of each acidic group in polymer phase.

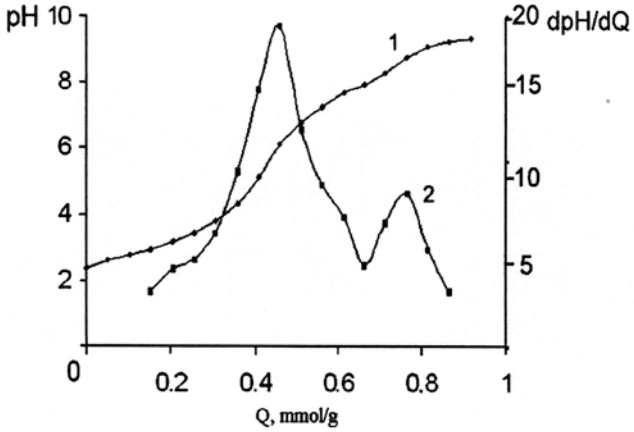

**Fig.1.** Integral (1) and differential (2) curves of potentiometric titration of sorbent.

Using α values and the corresponding pH data (tabl.1.) we plotted dependence diagram pH=*f*lg(α/(1-α)) (fig.2)

Table 1

**Ionization constants data for sorbent calculation**

| Ionization constant | pH | α | lg (α/1-α) | pK (graf.) | pK (calcul.) | | |
|---|---|---|---|---|---|---|---|
| | | | | | χ | $\overline{\chi}$ | $S_r$ |
| 1 | 2.74 | 0.16 | -0.72 | 4.4<br>n=3.23 | 5.07 | 4.405 | 0.005 |
| | 2.91 | 0.24 | -0.50 | | 4.53 | | |
| | 3.15 | 0.32 | -0.33 | | 4.22 | | |
| | 3.42 | 0.40 | -0.18 | | 4.00 | | |
| | 3.77 | 0.48 | -0.03 | | 3.87 | | |
| | 4.31 | 0.56 | 0.10 | | 3.99 | | |
| | 5.11 | 0.64 | 0.25 | | 4.30 | | |
| | 6.10 | 0.72 | 0.41 | | 4.78 | | |
| | 6.77 | 0.80 | 0.60 | | 4.83 | | |
| | 7.27 | 0.88 | 0.87 | | 4.46 | | |
| 2 | 7.92 | 0.16 | -0.72 | 8.64<br>n=0.70 | 8.42 | 8.638 | 0.002 |
| | 8.30 | 0.32 | -0.33 | | 8.53 | | |
| | 8.77 | 0.48 | -0.03 | | 8.79 | | |
| | 9.07 | 0.64 | 0.25 | | 8.90 | | |
| | 9.24 | 0.80 | 0.60 | | 8.82 | | |
| | 9.34 | 0.96 | 1.38 | | 8.37 | | |

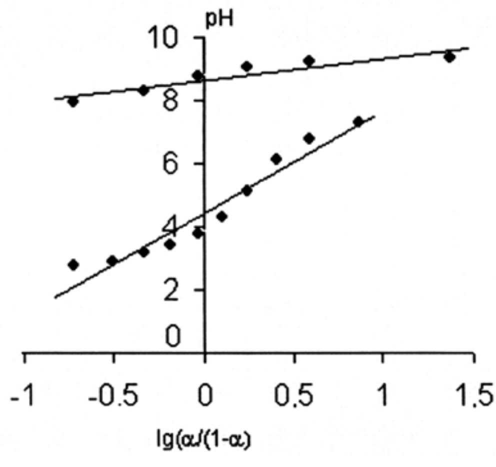

**Fig.2.** Graphical calculation of ionization constant of sorbent, where 1-$pK_1$=4.46; 2-$pK_2$=8.64.

As seen from Fig.2, this dependence has a linear character, but the slope ratio of a straight line (n- constant depending on the structure of the polymeric matrix and functional groups) differs from 1 ($n_1$=3.23; $n_2$=0.70), that can be explained by cooperative influence of functional groups on one another. Cooperativity lies in that that ionization constant of the functional groups of the sorbent depends on the degree of their neutralization. With the increase of the degree of neutralization of functional groups, the charge of the polymeric network increases and ionization of still not ionized functional groups becomes difficult.

Therefore for the calculation of apparent $pK_{ion}$ of active groups the Genderson-Gasselbach modified equation [8] has been used:

$$pK_{ion} = pH - nlg\frac{a}{1-a} \qquad (5)$$

where α is the neutralization degree of proton - containing groups of sorbent.

Thus, the values of ionization constants of functional groups of sorbents have been calculated according to the realized investigation: $pK_1$=4.46; 2-$pK_2$=8.64.

As seen from the achieved results, the values of the ionization constants of the obtained sorbent are within 2.1- 4.9 and 6.7-9.7 intervals, which are typical for the most PhCS [2].

While working with sorbents containing the same type of acid groups the main role belongs to medium acidity, defining state and reactivity of sorbent functional group. The metal ion state in solution also depends on medium acidity and it is possible by changing it to control the sorption process[8].

Therefore, in order to define the sorption properties of the investigated sorbent , at first the experiments on studying the dependence of sorption degree on pH solution in static conditions have been carried out.

Fig.3 presents the dependence of the copper ion sorption by sorbent on pH solution.

As seen from fig.3 the dependence of sorption degree on pH solution for the investigated copper ion has an external character. The relatively low sorption degree of metal ions in more acidic field ($pH \leq 2$) apparently due to the protonation state of sorbent in this field of pH has low swelling index. At that time sorption happens mainly as a result of ions, coordinating interaction with –P=O groups. However, these groups are also active centers for protons owing to hydrogen bonds formation –P=O....$H^+$, and that in its turn results in the displacement of metal ions from sorbent phase. In this acidity interval of aqueous solutions the metal is in the form of aqua complex ($[Cu(H_2O)_n]^{2+}$) [9].

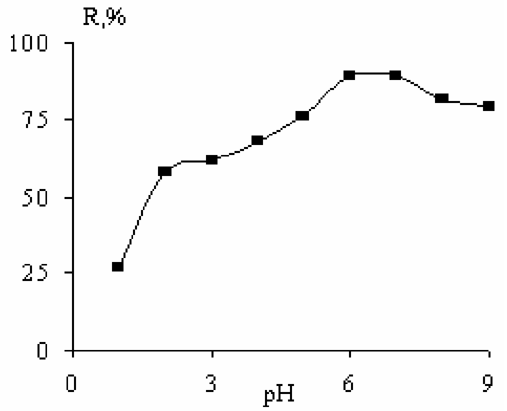

**Fig.3.** Dependence of copper ions sorption by sorbent on pH solution

With the decrease of solution acidity in the interval of pH=2-9, ions sorption gradually increases, reaches maximum and then decreases. Gradual ionization of functional groups of sorbents and partial transformation of existing aqua complexes to hydro complexes ($[Cu(OH)(H_2O)_{n-1}]^+$) take place in this field [9]. But in view that creation of pH≥3 medium has been realized due to the existing acetate-ammonium buffer in this field, the formation of both ammoniac and acetate complexes of different composition, structure and stability is possible. Reference analysis data indicates that the values of stability constants of ammonium complexes greatly exceed acetate stability constants, which allow us to neglect their formation in the investigated solutions [10]. Thus, copper ions at pH≥3 value will be present in the form of aqua, hydroxo- and ammonium complexes ($Cu(NH_3)_p^{2+}$), where p≥1. The ratio of these complexes differs for different values of pH mediums. The optimal value of copper ions sorption is obtained at pH, corresponding to that state of ions when ammonium complexes in the form of monoammine ($Cu(NH_3)^{2+}$) dominate in the solution. When pH value increases, the portion (quantity) in solution decreases. That can be considered as a reason of sorption decrease in alkalescent solutions.

Basing on findings further investigations have been done at pH 6, which correspond to $pH_{opt}$ for the investigated ions.

Sorption isotherm is the main characteristic of sorption capacity of any sorbent and presents the functional relation between the equilibrium concentration ($C_e$) and the equilibrium amount of sorbate ($C_a$). The analysis of sorption isotherms allows us to come to a certain conclusion about the surface character of sorbent, sorbat-sorbent interaction nature and so on [11].

The result of the investigation presented in fig.4 indicates that with an increase of initial concentration of sorbate its extraction degree also increases. 3 sites can be distinguished on the isotherm. Initial, abruptly rising upwards, almost linear site of the curve indicates that at low concentrations the sorption is practically proportional to this value (Henry site). At the same time the sorbates monolayer on the sorbent surface is formed.

Almost horizontal site, corresponding to great concentrations satisfies the surface of sorbents, completely saturated by sorbate. In these conditions if only monolayer of sorbate can be formed on the sorbent surface, the amount of sorbates practically ceases to depend on concentration. The middle site of the curve corresponds to intermediate degrees of fullness of the surface.

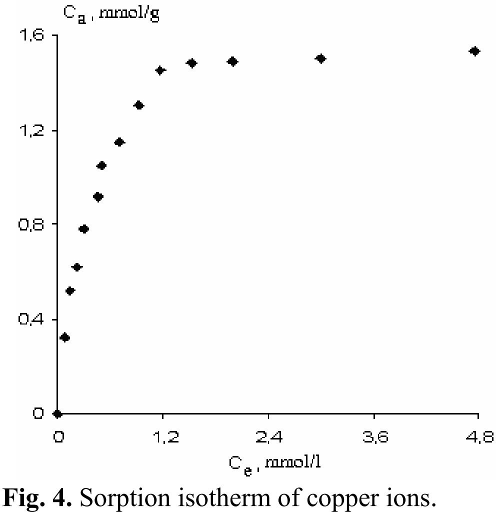

**Fig. 4.** Sorption isotherm of copper ions.

For mathematical description of the static equilibrium, formed in the sorption process Langmuir and Freundlich models have been applied [12-14].

Fig.5 and 6 present the sorption isotherm in the linear form.

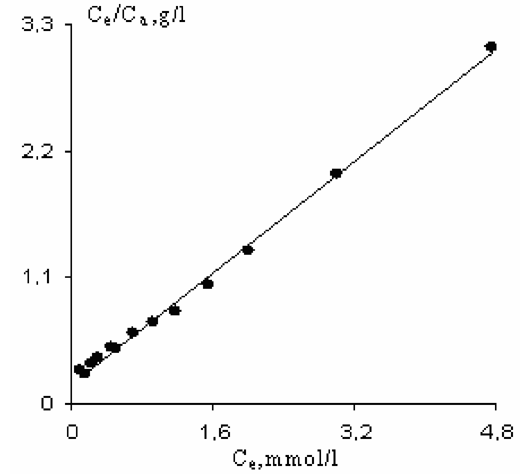

**Fig. 5.** Sorption isotherm of copper ions in the linear form by Langmuir.

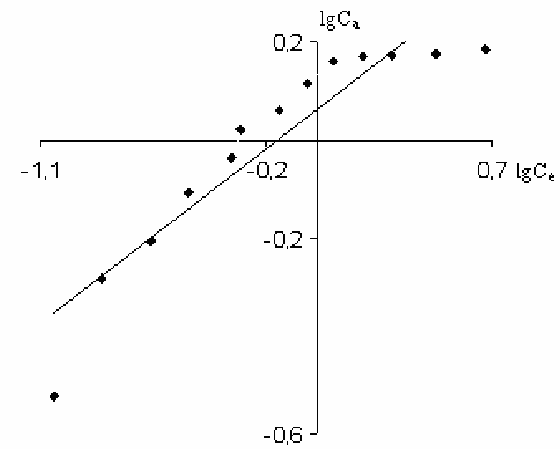

**Fig. 6.** Sorption isotherm of copper ions in the linear form by Freundlich.

The obtained constants and correlation coefficients have been summarized in table 2.

Table 2

**Constants of copper ions sorption isotherm**

| Langmuir models parameters | | | Freundlich models parameters | | |
|---|---|---|---|---|---|
| $a_{max}$, mmol/g | K, l/mmol | $R^2$ | $K_F$, (mmol/g)·(l/mmol)$^{1/n}$ | 1/n | $R^2$ |
| 1.659 | 3.279 | 0.9969 | 1.145 | 0.3 52 | 0.8642 |

As seen from table 2, the sorption isotherm is described better by the Langmuir equation than the Freundlich equation. This means that all sorbed particles only interact with sorption centers and don't interact with each other, therefore monomolecular sorption layer is formed on the sorbent surface.

Thus, the investigated sorbent is polyfunctional and can be used for copper ions removal from aqueous solutions.

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## POLİBUTADİEN ƏSASINDA SİNTEZ OLUNMUŞ FOSFOR TƏRKİBLİ POLİMER SORBENTİN FİZİKİ-KİMYƏVİ XASSƏLƏRİ

R.M.ALOSMANOV, A.Ə.ƏZIZOV, K.N.ORUCOVA,
İ.A.BÜNYADZADƏ, A.M.MƏHƏRRƏMOV

## XÜLASƏ

Təqdim olunan işdə polibutadien əsasında sintez olunmuş fosforsaxlayan polimer sorbentin potensiometrik titrləmə üsulu ilə turşu-əsas xassələri tədqiq olunmuş və mis ionlarına qarşı sorbsiya xassələri öyrənilmişdir. Sorbentin polifunksional olması təsdiqlənmiş, hər funksional qrup üçün $pK_{ion}$ hesablanmışdır. Müəyyən olunmuşdur ki, mis ionlarının maksimum sorbsiyası pH-ın 6 qiymətində müşahidə olunur. Sorbsiya izoterminin Lenqmyur və Frendlix modellərilə tədqiqi nəticəsində mis ionlarının energetik baxımdan bircinsli funksional qruplarda monomolekulyar təbəqənin yaranması ilə sorbsiyası sübut olunmuşdur.

# ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ФОСФОРСОДЕРЖАЩЕГО ПОЛИМЕРНОГО СОРБЕНТА НА ОСНОВЕ ПОЛИБУТАДИЕНА

**Р.М.АЛОСМАНОВ, А.А.АЗИЗОВ, К.Н.ОРУДЖЕВА,**
**И.А.БУНИЯТЗАДЕ, А.М.МАГЕРРАМОВ**

## РЕЗЮМЕ

В данной работе методом потенциометрического титрования исследованы кислотно-основные свойства фосфорсодержащего полимерного сорбента, полученного на основе полибутадиена и изучены сорбционные свойства по отношению к ионам меди. Выявлено, что исследуемый сорбент является полифункциональным и для каждого типа функциональных групп рассчитаны значения $pK_{ион}$. Установлено, что максимальная сорбция ионов меди наблюдается при pH=6. Изотерма сорбции, обработанная моделями Ленгмюра и Фрейндлиха, позволяет сделать вывод о том, что сорбция ионов меди происходит на энергетически однородных функциональных группах с образованием мономолекулярного слоя сорбата.