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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Simulation of Adsorption-Coagulation Purification of Liquid Radioactive Waste to Remove Surfactants

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Abstract—Sorption purification of liquid radioactive waste from special laundries of nuclear power plants to remove surfactants was simulated. The adsorption of an anionic surfactant, sodium dodecyl sulfate, on various carbon sorbents from complex-composition aqueous solutions containing mineral salts and complexing additives was studied.

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Utilization of radioactive waste is one of the most severe problems in modern nuclear power engineering. According to [1], the total volume of waste accumulated only in Russia by 2004 is about 600 million cubic meters, of which more than 250 thousand cubic meters is constituted by liquid radioactive waste (LRW) that is stored at nuclear power plants (NPPs) and requires deeper concentration to make more economically feasible its purification and utilization [2, 3].

A particular problem is posed by LRW from special laundries of NPPs, whose processing is complicated by their high content of surfactants, complexing additives [2, 4], and other components of detergents used in washing of working clothes. Various methods have been suggested for removal of these compounds: preliminary oxidation with potassium permanganate [5] or Fenton's reagent [6], ozonation [7], membrane purification [8, 9], electrocoagulation [10], and various adsorption techniques [11–15]. It has been shown previously that specially modified carbon sorbents based on OU-A activated carbon can be used for these purposes [16].

In adsorption purification of wastewater from special laundries of NPPs, it is necessary to take into account that surfactants contained in such LRW can spontaneously form in solutions hydrophilic aggregates, micelles, containing up to 100 surfactant molecules. The state of surfactants in solution (as separate molecules, ions, or associates of these) and their sorbability on carbon depend on various factors: nature of surfactants, concentration and temperature of their solutions, presence of electrolytes in solutions, etc. [17].

Real wastewater from special laundries and decontamination centers is constituted by complex aqueous solutions of variable composition, which contain, together with surfactants, protein particles, fats, $^{134,137}Cs$, ^{60}Co, and ^{90}Sr radionuclides, and nonradioactive mineral salts in amounts of up to 15 g dm^{-3}.

The goal of our study was to examine the adsorption of surfactants both from individual solutions and from solutions containing, together with surfactants, additions of mineral salts and complexing substances and to simulate on their basis the process of adsorption-coagulation removal of surfactants from aqueous solutions close in composition to LRW from special laundries of NPPs.

EXPERIMENTAL

We used carbon sorbents with large specific surface area and developed porous structure (Table 1): fibrous activated carbon of AUT-MI brand (Khimvolokno Republican Unitary Enterprise, Svetlogorsk, Belarus), powdered mineral activated carbon Silcarbon TH-90G

Table 1. Adsorption-structural characteristics of carbon sorbent

Sorbent	S_{sp}, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$		
		V_{mi}	V_{me}	V_{tot}
AUT-MI	1035	0.47	0.05	0.52
Silcarbon	950	0.44	0.11	0.55
OU-A:				
starting	920	0.39	0.15	0.54
modified	880	0.39	0.14	0.53

(Silcarbon Co., Germany), powdered activated charcoal of OU-A brand (Sorbent Open Joint-Stock Company, Perm, Russia), and modified sorbent produced in laboratory conditions from OU-A activated carbon [16, 18].

As anionic surfactant served 95% pure sodium dodecyl sulfate (SDS) manufactured by Sigma (Germany). The working concentrations of aqueous solutions of surfactants were in the range from 0.1 to 5.0 g dm^{-3}. To model LRW from special laundries of NPPs and examine the effect of various additives on the adsorption of SDS, we additionally introduced into solution cobalt nitrate hexahydrate and sodium nitrate and ethylenediaminetetraacetic acid (EDTA) and oxalic acid (chemically pure grade, Vekton Private Company, Russia).

Table 2. Effect of addition of mineral salts on the efficiency of removal of surfactants by the adsorption (A) and adsorption-coagulation (A/C) methods

Addition of a mineral salt	Purification method	Degree of surfactant recovery, %
No additives	A	86.0 ± 0.5
0.08 M $NaNO_3$	A	91.8 ± 0.5
2.0 M $NaNO_3$	A	93.0 ± 0.5
0.5 M $Co(NO_3)_2$	A	92.2 ± 0.5
No additives	A/C	92.5 ± 0.5
0.08 M $NaNO_3$	A/C	93.8 ± 0.5
2.0 M $NaNO_3$	A/C	94.0 ± 0.5
0.5 M $Co(NO_3)_2$	A/C	94.6 ± 0.5

To study the adsorption of anionic surfactants, we added 0.2 and 4.0 g of a carbon sorbent to 100 cm^3 of an SDS solution and agitated the mixture for 30 min at 25°C. After that the solid phase was separated with a blue-band paper filter, with the first 10 cm^3 of the filtrate discarded.

The content of surfactants and cobalt ions in purified water was determined by spectrophotometry, and EDTA, by complexonometric titration by the methods described in [19].

The specific adsorption Γ (mg g^{-1}) was calculated by

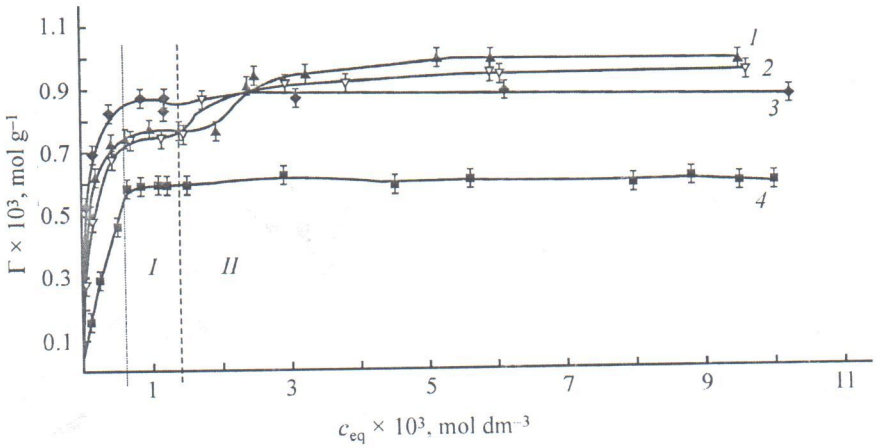

Fig. 1. Isotherms of SDS adsorption at 25 ± 0.1°C on activated carbons. (Γ) Specific adsorption and (c_{eq}) concentration. (*1*) Silcarbon. (*2*) OU-A, (*3*) modified OU-A, and (*4*) AUT-MI.

the formula

$$\Gamma = \frac{(c_{in} - c_{eq})V}{m} \times 10^3,$$

where c_{in} and c_{eq} are the initial and equilibrium concentrations of a component being analyzed in solutions (g dm^{-3}); V, solution volume (dm^3); m, mass of the sorbent (g).

When performing an adsorption-coagulation purification, we additionally treated, prior to filtration, the suspension produced by using the above scheme with a standard coagulant, $Al_2(SO_4)_3$, in an amount of 0.5 cm^3 of a 1% aqueous solution of the coagulant per 100 cm^3 of a suspension of carbon with the surfactant.

The adsorption of SDS from aqueous solutions on various carbon sorbents is described by high-affinity isotherms characterized by a high rate of increase in adsorption in their initial portions (Fig. 1). The isotherms of SDS adsorption on AUT-MI fibrous microporous carbon can be attributed to the Langmuir type with leveling off at equilibrium surfactant concentrations exceeding 0.65×10^{-3} mol dm^{-3} (Fig. 1, curve *4*). To the process of adsorption removal of SDS by other powdered carbons correspond step-like isotherms. In this case, the existence of the first plateau can be explained by the formation of a saturated monomolecular layer of SDS, and that of the second, by reorientation of surfactant molecules and changes in the structure of the adsorption layer [20].

Comparative analysis of the isotherms of SDS adsorption on various carbon sorbents indicates that

Table 3. Degree of recovery of SDS and Co:EDTA complex from aqueous solutions

Solution composition	Degree of recovery, %		
	SDS	EDTA	Co : EDTA complex
SDS (0.9 g dm^{-3})	99.5 ± 0.5	–	–
SDS (0.9 g dm^{-3}) + EDTA (1 g dm^{-3})	99.3 ± 0.5	94.8 ± 0.8	–
SDS + Co : EDTA (1 : 1)	99.3 ± 0.5	–	85.0 ± 2.0
SDS + Co : EDTA (1 : 1) + EDTA (1 g dm^{-3})	99.2 ± 0.5	80.1 ± 0.8	70.0 ± 2.0
SDS + Co : EDTA (1 : 1) + oxalic acid (1 g dm^{-3})	99.3 ± 0.5	–	66.0 ± 2.0
SDS + Co : EDTA (1 : 1) + $NaNO_3$ (15 g dm^{-3})	99.4 ± 0.5	–	85.0 ± 2.0
SDS + Co : EDTA (1 : 1) + EDTA (1 g dm^{-3}) + $NaNO_3$ (15 g dm^{-3})	99.2 ± 0.5	79.8 ± 0.8	70.0 ± 2.0

Table 4. Results of treatment of real LRW with a modified carbon sorbent[a]

LRW parameter	Still bottom from Kalinin NPP			Waste from Radon State Unitary Enterprise, Moscow Research-and-Production Association		
	before treatment	after treatment	decrease in parameter, times	before treatment	after treatment	decrease in parameter, times
Volume activity, Bq dm^{-3}:						
Σβ	35000	26000	1.4	18000	8700	2.1
Σα	–	–	–	250	3.8	65.8
Optical density	3.04	2.51	1.2	0.13	0.04	3.2
COD, mg O_2/dm^3	8000	40	200	125	<30	4.2

[a] Dosage of the carbon sorbent 5 g dm^{-3}.

activated carbons of OU-A and Silcarbon brands exhibit close adsorptive activities with respect to anionic surfactants in the whole range of surfactant concentrations under study (Fig. 1, curves *1* and *2*). The limiting amounts of adsorption coincide for these samples to within the experimental error. The modified OU-A also has close values of its adsorption characteristics (Fig. 1, curve *3*). The modified sorbent is more efficient in recovery of SDS from dilute solutions, and the starting unmodified OU-A carbon, in processing of micellar surfactant solutions with high content of organic substances. The data we obtained suggest that, under real conditions with consideration for the price factor, it is more appropriate to process LRW with carbons based on OU-A (starting and modified), whose cost is substantially lower than that of the German Silcarbon.

Presence of mineral salts in solution results in that micelles are formed at lower surfactant concentrations. It can be seen in Fig. 2 that presence of sodium and cobalt nitrates in an aqueous solution of SDS leads to a steeper decrease in the surface tension of a solution with increasing surfactant concentration and favors earlier formation of micelles. For example, the critical micelle concentration (CMC) found from the break in surface tension isotherms was 7.3×10^{-3} mol dm^{-3} for pure SDS at 25°C and a factor of 5 and 8 lower in 0.1 M solutions of sodium and cobalt nitrates (1.4×10^{-3} and 0.9×10^{-3} mol dm^{-3} for sodium and cobalt nitrates, respectively). The decrease in the CMC in the given case is due to suppression of the dissociation of ionogenic groups of the surfactant upon an increase in the ionic strength of the solution.

A study of the adsorption purification of aqueous solutions containing SDS, sodium nitrate, and cobalt nitrate with a modified OU-A demonstrated that presence of inorganic salts in an amount of 0.5–2.0 mol dm^{-3} not only does not impair the efficiency of the adsorption purification to remove surfactants, but even, by contrast, leads to an increase in adsorption by 10–20 mg g^{-1} (Fig. 3).

For fuller removal of SDS with the modified sorbent, which forms highly dispersed suspensions in water [18], it is advisable to additionally use a coagulant (Table 2). It was found that a high content of mineral salts (on the order of 100 g dm^{-3}) does not impair the efficiency of not only the adsorption purification of water, but of the adsorption-coagulation technique, either. The degree of

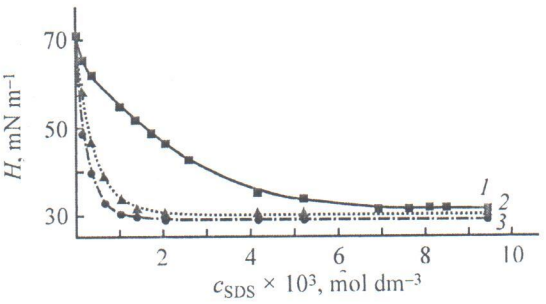

Fig. 2. Isotherms of surface tension H of aqueous solutions of SDS at 25.0 ± 0.1°C. (c_{SDS}) concentration. (*1*) No salt additives; additive: (*2*) 0.1 M $NaNO_3$ and (*3*) 0.1 M $Co(NO_3)_2$.

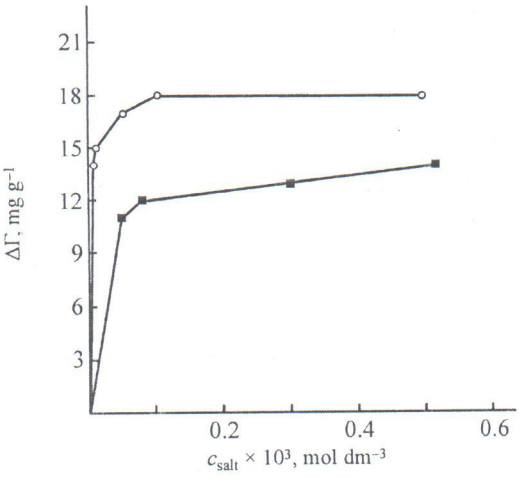

Fig. 3. Amount of SDS adsorption, $\Delta\Gamma = \Gamma^* - \Gamma_{SDS}$, vs. the concentration c_{salt} of inorganic salts. Salt: (*1*) $Co(NO_3)_2$ and (*2*) $NaNO_3$.

recovery of surfactants in a wide range of concentrations of sodium and cobalt nitrates is in this case not less than 90%. It was found in adsorption purification of solutions simultaneously containing SDS and Co^{2+} ions that presence of SDS in amounts exceeding the equimolar content of cobalt leads to an increased adsorption of this element. For example, despite that, according to published data, cobalt cations form no associates with anionic surfactants in aqueous solutions [21], the amount of cobalt adsorption at Co : surfactant ratios of 1 : 2 to 1 : 6 becomes eight times larger and reaches a value of 17.0 ± 2.0 mg g^{-1} (Fig. 4).

A study of solutions of more complex composition demonstrated that, at a sufficient amount of the sorbent

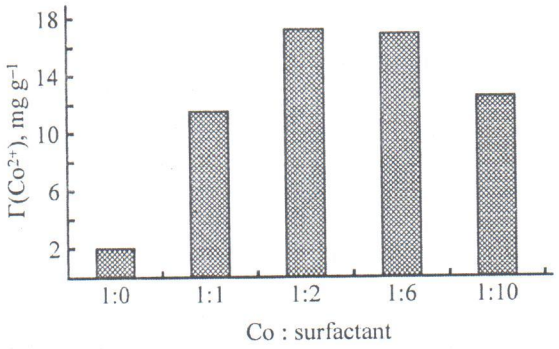

Fig. 4. Specific adsorption of Co^{2+} ions, $\Gamma(Co^{2+})$ vs. the Co : surfactant molar ratio.

(~40 g dm^{-3}), not only surfactants can be removed from LRW, but also complexing additives and organic compounds of cobalt (Table 3). For example, in joint presence of SDS and EDTA, the modified carbon sorbent can nearly fully remove these compounds from solution.

Introduction of cobalt ions into a solution of this kind is accompanied by formation of a stable Co : EDTA complex (*K*unst at 20°C is 7.9×10^{-17} [22]), which leads, in terms of individual components, to an increase in the adsorption of cobalt and to a decrease in that of EDTA. The latter can be accounted for by the architecture of the complex being formed, in which carboxy groups of EDTA are bound into a chelate structure with a cobalt cation at its center, which lowers energy of interaction between this complex compound and the sorbent surface. With increasing content of free EDTA, and also upon introduction of oxalic acid into the solution, the capacity of the carbon for the Co : EDTA complex decreases by approximately a factor of 1.2–1.3, which may serve as evidence that these compounds compete for active centers on the sorbent surface. The high degree of recovery of free EDTA in all the cases under study indicates that its adsorption is preferable as compared with the complex compound. At the same time, it follows from Table 3 that surfactants and mineral salts (in particular, $NaNO_3$) hardly affect the sorption of the Co : EDTA complex. In turn, the degree of SDS recovery at an excess amount of the sorbent remains nearly constant in all the cases we studied and reaches a value of 99.5 ± 0.5%.

The results of tests of the modified carbon sorbent on real LRW (Table 4), carried out at Radon State Unitary Enterprise, Moscow Research-and-Production Association, confirm that its use is advisable for utilization of LRW with high content of organic substances, whose amount was evaluated by the chemical oxygen demand (COD). It can be seen in Table 4 that treatment of the LRW under study with the modified carbon sorbent resulted in a fourfold decrease in the COD, i.e., organic substances hindering the conventional scheme of LRW purification are nearly completely removed, with the volume β-activity of the solutions and their total α-activity made 1.4–2.1 and 65 times lower, respectively.

CONCLUSIONS

(1) A study of the adsorption of surfactants from aqueous solutions modeling wastewater from special laundries at nuclear power plants on various carbon sorbents demonstrated that the most efficient and economically feasible for removal of surfactants are powdered carbon sorbents based on an activated carbon of OU-A brand.

(2) It was found that, at a sufficient amount of the sorbent, not only surfactants can be removed from liquid radioactive waste, but also complexing additives and organic compounds of cobalt. The adsorption recovery of cobalt is favored by the fact that it forms a complex compound with ethylenediaminetetraacetic acid.

(3) It was demonstrated that the suggested adsorption-coagulation technique will make it possible to substantially improve the purification efficiency of sewage from special laundries at nuclear power plants, to drop in some cases the presently used unsafe and expensive ozonation and poorly productive reverse osmosis stages, and to diminish the amount of ion-exchange resins necessary for full removal of radionuclides from liquid radioactive waste, with the amount of buried radioactive waste thereby reduced.

REFERENCES

1. Men'shikov, V.F., *Analiticheskii ezhegodnik "Rossiya v okruzhayushchem mire"* (Analytical Yearbook "Russia in the World Around"), Moscow: Modus_K-Eterna, 2005, pp. 81–127.
2. Kul'skii, L.A., Strakhov, E.B., and Voloshinova, A.M., *Tekhnologiya vodoochistki na atomnykh energeticheskikh ustanovkakh* (Technology of Water Purification at Nuclear Power Installations), Kiev: Naukova Dumka, 1986.
3. Shul'ga, N.A. and Sokolova, I.D., *Atomn. Tekhn. Rubezh.*,

2008, no. 9, pp. 3–19.

4. Guerrero, A., Gosi, S., and Allegro, V.R., *J. Hazard. Mater.*, 2009, vol. 161, nos. 2–3, pp. 1250–1254.
5. Rudenko, L.I., Dzhuzha, O.V., and Khan, V.E., *Dopovidi Nats. Akad. Nauk Ukr.*, 2008, no. 5, pp. 151–154.
6. Perkowski, J., Juuwiak, W., Kos, L., and Stajszczyk, P., *Fibres Text. East. Eur.*, 2006, vol. 14, no. 5, pp. 114–119.
7. Omel'chuk, V.V., Stakhiv, M.R., Savkin, A.E., et al., *Bezopasn. Okruzh. Sredy*, 2007, no. 3, pp. 34–38.
8. Demkin, V.I., Adamovich, D.V., Amelin, V.S., and Panteleev, V.I., *Kritich. Tekhnol., Membr.*, 2002, no. 15, pp. 10–13.
9. Pabby, A.K., *Membr. Technol.*, 2008, vol. 2008, no. 11, pp. 9–13.
10. Onder, E., Koparal, A.S., and Ogutveren, U.B., *Separ. Purif. Technol.*, 2007, vol. 52, no. 3, pp. 527–532.
11. Myasoedova, G.V. and Nikashina, V.A., *Ros. Khim. Zh.*, 2006, no. 5, pp. 55–63.
12. Matsuo, T. and Nishi, T., *Carbon*, 2000, vol. 38, no. 5, pp. 709–714.
13. Omar, H.A. and Moloukhia, H., *J. Hazard. Mater.*, 2008, vol. 157, nos. 2–3, pp. 242–246.
14. Shilina, A.S. and Melenchuk, V.K., *Izv. Vyssh. Uchebn. Zaved., Yadern. Energet.*, 2008, no. 3, pp. 24–30.
15. Maslov, A.A. and Avsaragov, Kh.B., *Vestn. Mosk. Gos. Tekh. Univ.*, 2007, vol. 10, no. 4, pp. 621–623.
16. Grinshpan, D.D., Ivanets, M.G., Bakhir, N.K., et al., *Bezopasn. Zhiznedeyat.*, 2009, no. 9, pp. 13–17.
17. Lange, K.R., *Poverkhnostno-aktivnye veshchestva: Sintez, svoistva, analiz i primenenie* (Surfactants: Synthesis, Properties, Analysis, and Application), St. Petersburg: Professiya, 2007.
18. Savitskaya, T.A., Nevar, T.N., and Grinshpan, D.D., *Kolloid. Zh.*, 2006, vol. 68, no. 1, pp. 1–7.
19. Lur'e, Yu.Yu., *Analiticheskaya khimiya promyshlennykh stochnykh vod* (Analytical Chemistry of Industrial Wastewater), Moscow: Khimiya, 1984.
20. Koganovskii, A.M. and Klimenko, N.A., *Fiziko-khimicheskie osnovy izvlecheniya poverkhnostno-aktivnykh veshchestv iz vodnykh rastvorov i stochnykh vod* (Physicochemical Foundations of Removal of Surfactants from Aqueous Solutions and Wastewater), Kiev: Naukova dumka, 1978.
21. Chernova, R.K., *Izv. Saratov Univ., Khim., Biol., Ekologiya*, 2005, vol. 5, no. 1, pp. 33–40.
22. *Kratkii spravochnik fiziko-khimicheskikh velichin* (Concise Reference Book of Physicochemical Constants), Moscow: SpetsLit, 1998.