STUDIES ON THE SORPTION PROPERTIES OF NATIVE SORBENTS

First report

Thermal Activation of Native Sorbents from North-Eastern Bulgaria for Rendering Innocuous the Nickel Ions from Industrial Sewage Waters

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Native sorbents comprise a number of natural materials which possess, without any preliminary treatment, a substantially high adsorption capacity as regards vapours, liquids or dissolved substances. The latter quality of the materials referred to is connected with the porosity of their structure, which, in turn, conditions their highly developed surface. According to V. T. Bikov and co-workers (7, 8), the characteristics of the surface of sorbents of natural origin represents the factor upon which adsorption and chemical binding (hemosorption) largely depend. These sorbents are widely spread in nature. They include bleaching clays (hydrated aluminum silicates), active earth (silicolites), natural chemical deposits (boxite, laterite, ferrolite and others), organic sediments (in lakes, seas and oceans) and organic formations (natural products with vegetable and animal origin: humus, peat, lignithis etc).

The diversity of the conditions of formation mineral species, possessing high adsorptional properties, accounts for qualitative variety of the natural sorbents which, according to E. Gauser and D. Lebeaux (10), are hardly inferior to the artificially prepared sorbents. The above circumstance, in conjunction with the low cost and availability of native sorbents allows our national economy to utilize them in accordance with their specific qualities. Hence the extensive and systematic investigation of the physicochemical and adsorptional properties of natural mineral sorbents is fully justified and expedient.

It is a well known fact that natural sorbents find a wide scope of application for a variety of purposes, such as sanitary water purification, regeneration of pre-treated waters, purification of organic materials, extraction of expensive and rare metals, in drug stuffs preparation etc. Moreover, they replace imported and very expensive sorbents with cheap, locally available natural materials.

In this country, although in somewhat limited scale, studies are in course on the properties of Bulgarian native sorbents. In this respect, considerable contributions have been made by D. Dimitrov and assoc. (1),

D. Milev and S. Kuyumdjiev (2), Tz. Obretenov (3), I. Radev and Zahariev (4), R. Teneva (5, 6). T. Trendafilov and L. Tomassini (18) investigated, more particularly, the sorption capacity of the Dimitrovgrad and Kardjali bentonite towards drug stuffs. Hitherto, in this country, no studies have been conducted on the possibilities of using native sorbents for sanitary-hygienic aims.

In a number of industrial enterprises, various kinds of sewage waters, polluted equally by organic and inorganic substances, are produced. Pollutions of organic origin are particularly dangerous from the viewpoint of public health. For instance, they could by no means be employed for irrigation and other purposes. On the other hand, the consumption of industrial and potable waters is rapidly increasing, parallel to the development of industry and population growth. The construction of purifying stations and facilities lags behind the intensive industrial build-up. There are purifying stations and facilities available in many factories but the efficiency of their utilization is very low. That is why the problem of sanitary water purification in this country appears to be most pressing.

It is generally known that in the process of purification, not merely adsorption plays a role, as a number of sorptional processes are mutually interweaved, such as adsorption, capillary condensation, hemosorption and colloid chemical processes. Hence, we undertook the task to investigate systematically the sorption properties of native sorbents from North-Eastern Bulgaria in terms of different organic and inorganic substances. Moreover, no reference was found in the pertinent literature concerning the sorption properties of native sorbents from this particular region. In the case referred to, we considered more particularly the binding potential of Ni^{2+} in industrial sewage waters from galvanic plating enterprises, wherein valuable materials are eliminated, such as Ni, Au, Ag, Cr etc.

There are cases in the routine practice of Ni^{2+} determination in various media at the exclusive utilization of expensive materials. Thus, Y. V. Morachovski and co-workers (11) employed anionites PZK and PZ-9 in Cl-form for separating Ni^{2+} from Zn^{2+}. T. B. Gapon and E. N. Gapon (9) synthesized permutite and studied its adsorption capacity as regards Ni^{2+} and Co^{2+}. N. K. Pshenitzin and co-workers (12) retained Ni^{2+} over Cu-1. To extract Ni^{2+} from sewage waters, S. M.Chernobrov and co-workers (14) used hydrogen sulphide and ion exchange resin KB-2. R. H. Herber and co-workers (15), K. Kraus and G. Moore (16), Ch. Miller and A. Hunter (17) and others also employed ion exchange resins.

The native sorbents, after adequate treatment—thermal or chemical — may acquire high adsorption capacity, due to alterations in their composition and structure. Native sorbents, processed in this manner, might substitute very successfully the expensive synthetic sorbents (13). Among the various types of native sorbents' activation, the thermal one is cheaper and simpler for execution. Owing to the latter reasons, in the present work we deal merely with thermal activation. White bentonite from Balchik, clay from the village of Loznitza, district of Silistra, motor probe 4 (MS-4) and motor probe 27 (MS-27), district of Silistra, were used as study objects.

Preparation of the sorbents for activation was carried out in the following manner: the crude sorbents are dried at 105° C in a drying room. About 500—600 g of the samples are ground separately in a ball grinder for a duration of 2—3 hours. Next, through a sieve with diameter of the openings 0.10 mm, the fine fraction is separated and thereby subjected to activation.

Thermal activation is carried out at several different temperatures: 105°, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500° and 600° C. About 30 g sorbent is placed in a porcelain crucible and heated up in a muffel furnace for five hours at the respective temperature. Thereafter it is removed, cooled somewhat, transferred in a volumetric flask, plugged tightly and placed in an exsiccator for tempering up to room temperature. The samples thus treated are ready for sorption.

We chose sorption at static conditions which was executed in the following fashion: one gram of each sorbent is weighed out and placed in a flask, poured over with 25 cc of the respective solution and kept for 24 hours (stirring from time to time). This is enough time for attaining the equilibrium desired. After that, it is filtered and the filtrate is subjected to analysis. Under static conditions, a possibility is provided for continuous contact between the sorbent and the solution. Stirring also contributes for a better sorption since it exerts effect on the concentrational gradient.

$NiSO_4$ solutions at concentrations 0.033, 0.066, 0.1, 0.133, 0.166 % Ni^{2+} were used as model solutions. The listed above concentrations of the model solutions correspond to the Ni^{2+} concentrations in the sewage waters of some of our industrial enterprises.

Ni^{2+} determination was performed with spectrophotometer «Jouan». For the purpose it is necessary to secure 1 % alcohol solution of dimethyl-glyoxim, saturated bromic water and 4 n ammonium. Determination proper runs the following course: the solution undergoing analysis, containing less than 150 mKg nickel (in our case 2 cc of the filtrate), is placed in a volumetric flask of 100 cc volume, and then bromic water is added until a yellow tinge appears. After 10 min, ammonium solution is added, initially by dripping, till disappearing of the bromine stain, and thereafter supplemented by 20 cc ammonium solution and 10 cc dimethyl-glyoxim solution. It is diluted with distilled water up to the measuring point, stirred and within 15 min, the optical density of the solution is measured at $\lambda=465$ nm (19). The nickel content is computed by the calibrated curve. Standard solution with variable concentration of nickel ions is used for the setting up of the calibrated curve, which reflects the relationship between light-adsorption (E) and nickel ions' concentration.

The results of the study are presented in tables 1, 2, 3, 4 and 5.

Table 1

Ni^{2+} Sorption from Solution with Concentration 0.033% Ni^{2+} over Native Sorbents from North-Eastern Bulgaria in mg/g Sorbent

Sorbent	Temperature in °C									
	105	150	200	250	300	350	400	450	500	600
Bentonite from Balchik	8.25	8.25	8.17	8.21	8.25	8.10	8.17	8.02	7.96	7.83
Clay from Loznitza	8.25	8.25	8.17	8.25	8.09	8.25	8.17	8.10	8.02	7.96
MS-4	8.25	8.25	8.19	8.25	8.26	8.27	8.26	7.96	7.93	7.80
MS-27	8.25	8.25	8.22	8.22	8.25	8.25	8.10	7.94	7.91	7.88

Table 2

Ni^{2+} Sorption from Solution with Concentration 0.066% Ni^{2+} over Native Sorbents from North-Eastern Bulgaria in mg/g Sorbent

Sorbent	Temperature in °C									
	105	150	200	250	300	350	400	450	500	600
Bentonite from Balchik	16.5	16.31	16.5	16.35	16.5	16.30	16.35	16.2	16.17	16.02
Clay from Loznitza	16.5	16 42	16.41	16.39	16.3	16.42	16.32	16.29	16.19	15.94
MS-4	16.46	16.42	16.42	16.50	16.50	16.5	16.39	16.21	16.11	15.94
MS-27	16.5	16.4	16.42	16.39	16.5	16.5	16.29	16.35	16.15	16.00

Table 3

Ni^{2+} Sorption from Solution with Concentration 0.1% Ni^{2+} over Native Sorbents from North-Eastern Bulgaria in mg/g Sorbent

Sorbent	Temperature in °C									
	105	150	200	250	300	350	400	450	500	600
Bentonite from Balchik	24.89	24.79	24.85	25.0	24.8	25.0	24.85	24.85	24.79	24.69
Clay from Loznitza	25.0	25.00	25.0	25.0	24.97	25.0	24.79	24.85	24.75	24.60
MS-4	25.0	24.94	25.0	25.0	24.81	25.0	24.83	24.79	24.69	24.47

It is obvious from the data submitted in the tables that there exists an optimal temperature regimen for thermal activation of the four native sorbents, ranging between 200 and 400° C. At 0.033% Ni^{2+} concentration, the sorbents attain maximum sorption during thermal treatment at 350° C. The same holds true for 0.1% Ni^{2+} concentration. At 0.066% concentration of the nickel ions, maximum adsorption is reached at 300° C. At high tem-

Ni^{2+} Sorption from Solution with concentration 0.133% Ni^{2+} over Native Sorptions from North-Eastern Bulgaria in mg/g Sorbent

Table 4

Sorbent	Temperature in ° C									
	105	150	200	250	300	350	400	450	500	600
Bentonite from Balchik	32.89	32.89	33.01	33.06	33.25	33.25	33.04	32.96	32.86	32.76
Clay from Loznitza	33.25	33.17	33.14	33.25	33.22	33.22	33.24	32.92	32.81	32.60
MS-4	33.17	33.04	33.17	33.25	33.10	33.17	33.00	32.92	32.81	32.70
MS-27	33.17	33.10	33.10	33.25	33.25	33.25	33.10	33.04	32.92	32.70

Table 5

Ni^{2+} Sorbtion from Solutions with Concentration 0.166% Ni^{2+} over Native Sorbents from North-Eastern Bulgaria in mg/g Adsorbent

Sorbent	Temperature in ° C									
	105	150	200	250	300	350	400	450	500	600
Bentonite from Balchik	40.81	40.80	40.91	41.24	41.21	41.39	41.29	41.29	40.80	39.97
Clay from Loznitza	41.46	41.29	41.44	41.46	41.41	41.37	41.25	41.27	39.97	39.81
MS-4	41.35	41.35	41.27	41.35	41.50	41.39	41.25	41.29	40.02	39 86
MS-27	41.35	41.35	41.35	41.50	41.39	41.50	41.29	41.17	40.00	39.65

peratures of the order 400° C, the sorbents do not increase their sorption properties. Presumably, at temperatures slightly exceeding 575°, the sorption capacity would be improved at the expense of the polymorphic transformation of beta-quartz into alpha-quartz. Since the latter phenomenon was not observed, it is evident that despite the considerable SiO_2 content in the native sorbents investigated, in this particular case the polymorphic transformations failed to exert any influence upon the sorption capacity of the sorbents, regardless of the volume alterations ensuing.

Inferences

As the concentrations of the model solutions are in conformity with the Ni^{2+} concentrations in the draining waters of the industrial enterprises in this country, it is evident that the native sorbents studied are suitable for binding and consequently, rendering innocuous Ni^{2+}. For the purpose, preliminary thermal activation is required at temperature ranging from 200 to 400° C, which is readily attained under the conditions existent in many of the factories with shops for galvanic plating (Elprom and Metal — Varna). Particularly favourable in this respect appears to be the bentonite from Balchik. Equally good results were disclosed by the clay from the village of Loznitza, district of Silistra. No doubt that both native sorbents, activied at temperature ranging from 200—400° C are feasible for sanitary-hygienic elimination of Ni^{2+} from the sewage waters, produced by the industrial enterprises in this country. Owing to being readily available and to the insignificant cost of thermal activation, their application would hardly meet any difficulties and furthermore, it would be expedient and economically beneficial.

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ТЕРМИЧЕСКОЕ АКТИВИРОВАНИЕ ПРИРОДНЫХ СОРБЕНТОВ ИЗ СЕВЕРО-ВОСТОЧНОЙ БОЛГАРИИ В ЦЕЛЯХ ОБЕЗВРЕЖИВАНИЯ ЙОНОВ НИКЕЛЯ В ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОДАХ

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РЕЗЮМЕ

Природные сорбенты после подходящей обработки, термической или химической, могут приобрести высокую сорбционную способность, что обусловлено изменением их состава и структуры. Обработанные таким образом сорбенты могут с большим успехом заменить дорого стоящие синтетические сорбенты.

В настоящей работе изучено термическое активирование бентонита из г. Балчика, глины из с. Лозницы, Силистренского района, глины моторного зонда 4 (МЗ-4) и моторного зонда 27 (МЗ-27) в Силистренском районе, и сорбция Ni^{2+} на них из растворов с различной концентрацией Ni^{2+}.

Высушенные при 105° С сорбенты перемалывали в шаровой мельнице и просеивали через сито с диаметром отверстий, равным 0,10 мм.

Термическое активирование осуществлялось при температурах 105, 150, 200, 250, 300, 350, 400, 450, 500 и 600° С. Сорбцию проводили с модельными растворами $NiSO_4$ с концентрациями 0,033, 0,066, 0,10, 0,133, 0,166% Ni^{2+}, соответствующими концентрациям Ni^{2+} в сточных водах промышленных предприятий. Полученные результаты сведены в пять таблиц.

Было установлено, что полученные природные сорбенты пригодны для очистки сточных вод. Хорошие результаты получены при термической обработке при температурах между 200 и 400° С. При концентрации 0,033% Ni^{2+} у сорбентов отмечался максимум сорбции при термической обработке при 350° С. То же самое касается и концентрации 0,1%. При температурах выше 400° С сорбционные качества сорбентов не повышаются.