ADSORPTION OF METHYLENE BLUE OVER SOME ACID AND THERMALLY ACTIVIED NATIVE SORBENTS IN ULTRASOUND FIELD

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The rapid development of industry poses with steadily increasing urgency the problem of rendering innccuous the various toxic substances contained in sewage waters. The solution of the problem thus outlined is connected with the introduction in practice of hitherto unemployed raw-material sources, subsequent to their beforehand mechanical and chemical treatment.

Such raw materials include the native sorbents which in the crude state, have low sorption capacity. In our industry, as yet imported sorbents are being used which are comparatively expensive. All this necessitates the search for ways of improving the properties of our natural sorbents. On the first place, the question is confronted of establishing adequate preliminary processing of the sorbent, which would provide for the attaining of maximal sorption capacity.

In the special literature a number of publications have been made, referring to various issues of natural sorbents' activation (3,4). In this country too, similar investigations have been carried out, some of which concerning the sorption of methylene blue over native adsorbents (1).

In modern technology, one of the new physical methods for the intensification of chemical processes used is the method based on elastic fluctuations with sound and ultrasound range of the frequency. Heretofore, the opinion that the use of ultrasound on national industry scale is rather expensive has been predominating. The latter fact was explained with the imperfection of the ultrasound apparatus and equipment in use. The utilization of up-to-date ultrasound facilities, apart of being efficient, also accounts for substantial economies (5, 6).

The present work deals with the results of investigating the sorption properties of clay from the city of Kardjali as regards methylene blue water solutions.

The sorbent under study underwent two types of treatment — acid or thermal. Prior to treatment, the crude sorbent is ground finely in a ball grinder and sifted through a sieve with diameter of the openings $0.08 \times \times 10^{-3}$ m (mesh). The acid activation method consists in the following: about 30×10^{-3} kg sorbent is placed in volumetric flasks of 250 ml and poured over with 150 ml 2, 5, 10 and 20% hydrcchloric acid. Following intense stirring till full mixture, it is kept for two days with stirrings perfcrmed periodically. Thereafter it is filtered through a Büchner funnel and rinsed with distilled water until negative reaction for chlorine ions with respect to

silver nitrate occurs. After the washing, the sorbent is dried at 105° C and preserved in exsiccator.

Thermal activation of the sorbent is carried out by heating it up in porcelain crucibles for a duration of five hours at 105°, 125°, 175°, 200°,

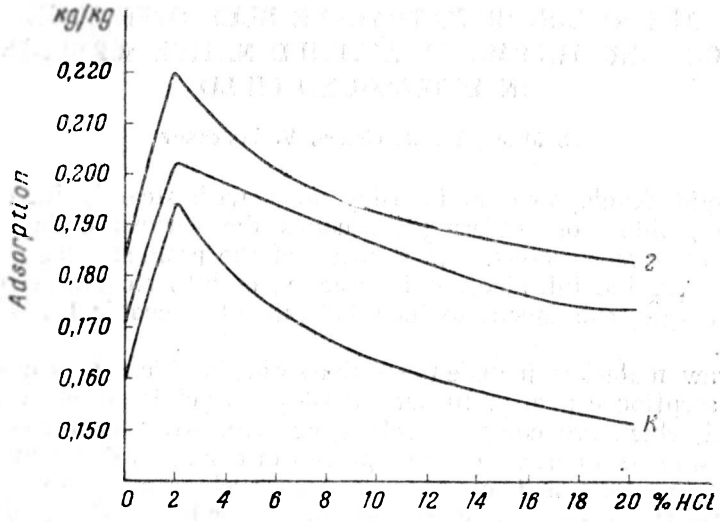

Fig. 1

250°, 300°, 350°, 400°, 450°, 500°, 550° and 600° C. Tempering is performed in a muffel furnace and after that the ready samples are conserved in an exsiccator.

Methylene blue solution is prepared by dissolving 1.6×10^{-3} kg in one liter distilled water and keeping it for 24 hours with intermittent stirring.

The sorption capacity of the samples as regards methylene blue water solutions was determined after the method of R. Robertson and R. M. Ward (7). In 250 ml volumetric flasks, 0.2 to 0.3×10^{-3} kg sorbent of the respective sample is placed and poured over with 40 ml solution of methylene blue. The flask is stirred intensively for a period of 20 min, kept for 10 min and centrifuged at 2500 rev/min for five minutes. From the centrifuge, with the aid of FEK-56, and in compliance with the previously set up calibrating curve, the methylene blue concentration is established (2). The samples from sorbents activied in different ways were subjected to ultrasound effect according to the above description. Instead of stirring the flask for 20 minutes, it was placed for the identical period of time in ultrasound field at frequency 22 кHz and 800 kHz and intensity of the field, respectively 4 W/cm² and 3 W/cm².

Tables 1 and 2 illustrate the results of the experimental studies. The same results are presented graphically in Figures 1 and 2.

It is evident from the data submitted in Table 1 and Fig. 1 that the lowest sorption capacity is recorded in crude, untreated sorbent, whilst the highest sorption capacity is disclosed by the sorbent treated with ultra-

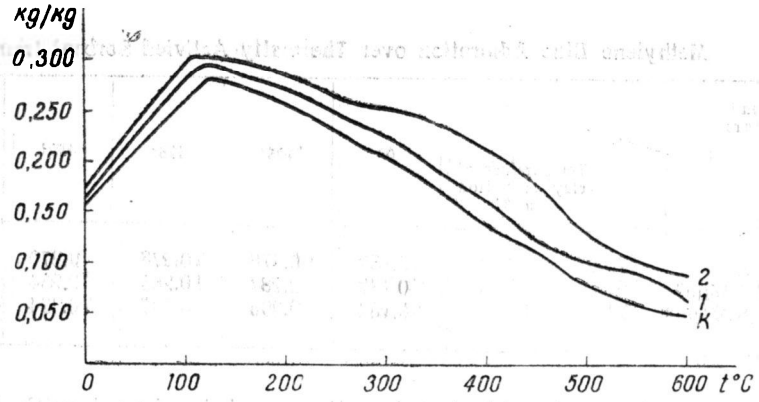

Fig. 2

Table 1

Methylene Blue Adsorption over Activied Sorbent from the City of Kardjali in Ultrasound Field in Kg/Kg Sorbent

Ultrasound parameters / Percentage of HCl	0%	2%	5%	10%	20%
Control	0.159	0.194	0.175	0.163	0.152
22 kHz 4 W/cm²	0.172	0.202	0.196	0.186	0.174
800 kHz 3 W/cm²	0.189	0.219	0.204	0.192	0.183

sound at 800 kHz (Fig. 1, curve 2). Moreover, it is obvious that the maximal sorption capacity is obtained during acid treatment with 2% HCl, and after the latter concentration, a tendency for reduction is manifested. Thus, the percentual expression of the latter facts would be as follows: the sorption capacity of the sample activied with 2% HCl and subjected to ultrasound treatment at 800 kHz is with about 12% higher than that activied with 2% HCl only and untreated with ultrasound (control), whilst the sorption capacity of the sample activied with 2% HCl and ultrasound at 22 kHz is about 4% higher than the control (the same but untreated with ultrasound). The sorption capacity of the sample activied with 2% HCl and subjected to ultrasound treatment with 800 kHz, as compared to crude, untreated sorbent, shows an increase with about 38 per cent. Figure 2 demonstrates that the highest sorptional capacity occurs at 125° C thermal processing of a sample, combined with ultrasound treatment at 800 kHz, being about 7% that of the sample activied at 125° C and not subjected to ultrasound treatment (control). The sorption capacity of the sample

Methylene Blue Adsorption over Thermally Activied Sorbent from Kardjali

Ultrasound parameters / Temperature of clay activation in °C	0°	105°	125°	150°	175°
Control	0.159	0.276	0.278	0.270	0.262
22 kHz 4 W/cm²	0.172	0.284	0.288	0.284	0.270
800 kHz 3 W/cm²	0.184	0.293	0.297	0.294	0.288

activied at 125° C and subjected to ultrasound treatment with 800 kHz (Fig. 2, curve 2) is 87% higher as compared to the crude (non activied) sorbent (Fig. 2, curve k). As illustrated in Fig. 2, following activation at temperature 125° C, the sorptional capacity is quickly reduced, reaching values much lower than the initial ones (non-activied samples).

Summarizing the table data and curves' course, it is beyond any doubt that the ultrasound field exerts a positive effect on the sorptional properties of the samples under investigation.

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Table 2

and Control, Expressed in Kg/Kg Sorbent

200°	250°	300°	350°	400°	450°	500°	550°	600°
0.253	0.229	0.202	0.170	0.135	0.108	0.077	0.059	0.048
0.270	0.229	0.221	0.190	0.158	0.117	0.102	0.091	0.063
0.281	0.267	0.236	0.236	0.210	0.174	0.120	0.098	0.084

АДСОРБЦИЯ МЕТИЛЕНОВОЙ СИНИ НА НЕКОТОРЫХ СОРБЕНТАХ ПОСЛЕ ИХ КИСЛОТНОГО И ТЕРМИЧЕСКОГО АКТИВИРОВАНИЯ В УЛЬТРАЗВУКОВОМ ПОЛЕ

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РЕЗЮМЕ

В работе приведены результаты изучения сорбции метиленовой сини на природном сорбенте из г. Кырджали в ультразвуковом поле.

Сорбент активировали 2, 5, 10 и 20%-ной соляной кислотой и термически при температурах 105, 125, 175, 200, 250, 300, 350, 400, 450, 500, 550 и 600° С. В водном растворе метиленовой сини содержится $1{,}6.10^{-3}$ Kg метиленовой сини в литре. Сорбционную способность определяли методом R. Robertson и R. M. Ward при использовании 0,2 до $0{,}3.10^{-3}$ Kg сорбента для каждого определения. Работали при ультразвуковом поле с частотой 22 кгц и 800 кгц и интенсивнссти 4 вт/см^2 и 3 вт/см^2. Полученные результаты отражены в двух таблицах и двух диаграммах.

Было установлено, что в общем ультразвуковое поле оказывает положительное воздействие на сорбционные свойства активированных поразному образцов.