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STUDIES ON THE YIELD OF FATTY IMPURITIES SEPARATION FROM BLEACHING EARTH BY EXTRACTION METHOD

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ABSTRACT

The method of vegetable oil bleaching by adsorption of impurities using activated bentonite involves the necessity of its regeneration. Studies on the yield of fatty impurities extraction by ethanol, isopropanol at the temperatures 35; 50; 65^{o}C in alkaline medium at NaOH or KOH concentration range from 0.015 to 0.415 mole/dm^3 of alcohol have been carried out. It was shown that ethanol solution with 0.323 mole/dm^3 NaOH concentration is excellent extraction solvent.

Keywords: fatty impurities; bleaching earth; recycling; extraction

INTRODUCTION

The oiled bleaching earth is a waste material in the fat industry which can be easily recirculated [1] with possibility to recover fatty substances and material which can be used after regeneration as an adsorbent [2, 3]. This operation is most often forced by legal regulations concerning environmental protection. The authorities taking decisions of macroeconomic importance (e.g. valid systems of waste disposal) more and more often are governed by basic ecological criteria such as: reduction of power and raw materials consumption, decrease of dangerous substances in air and water as well as keeping to a minimum the wastes stored on dumping grounds [4, 5].

The bleaching earth is an adsorbent for bleaching the oil. The used bleaching earth is a solid waste (fat industry in Warsaw produces

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approximately 1300 tons of oiled bleaching earth per year [6]) containing up to 40% of fat depending on the method of the filtrated adsorbent squeezing out. 1 kg of adsorbent costs about 3.5 $, therefore its recovery is an important problem especially in the aspect of ecobalance.

The process can be realized applying various technologies. The simplest one consists in boiling-out the earth with soda lye [7], but this process is technologically burdensome. The method consisting of extraction with hexane [8, 9] can be applied in large refineries in which production achieves 6 tons of the oiled adsorbent per day. These methods are not applied in Poland because of economic reasons. Therefore, studies on the development of effective and cheap methods of bleaching earth recirculation should be undertaken.

In this paper, the preliminary investigations on selection of the effective medium for extraction of waste oil from bleaching earth have been carried out. The alkaline hydrolysis reaction of fat gives soaps, which are surfactants so they increase the effectiveness of extraction process. It was decided to use the alcoholic lye solution – alcohols are solvents for lye and fatty waste at the same time.

METHODS

Apparatus and chemicals applied

Bleaching earth. The oiled bleaching earth from Fat Plant "Kruszwica" Co. (Poland) was applied for our studies. Activated natural betonite (TONSIL OPTIMUM 210 FF produced by Süd-Chemie AG, Germany) was used as adsorbent.

Solvents. The following alcohols were applied as solvents:

- ethanol containing 0.165 mole/l, 0.323 mole/l and 0.415 mole/l of soda lye, respectively;
- n-butanol - pure and containing potassium hydroxide in amounts of 0.015 mole/l and 0.118 mole/l;
- isopropanol - pure and containing potassium hydroxide in amounts of 0.015 mole/l and 0.118 mole/l.

The following experimental method was accepted:

Extraction by shaking and decantation was performed in thermostating apparatus i.e. drier with adjustable temperature and all the reagents, materials and laboratory glass were kept at a suitable temperature (35, 50, 65^{o}C) during the process, so that precipitation of fat from extract could not occur. The required elements were taken out of the drier only for shaking and sampling and after operation they were put into the drier again. The flasks used for extraction were closed with stoppers in the aim to make evaporation of solvent impossible. The content of sodium or potassium base was determined in extracts by titration with hydrochloric acid (0.1 mole/l) in the presence of methyl orange.

Extraction was performed by the method described below.

Ten grams of the oiled adsorbent were weighed with accuracy to 1 mg and put into each of five dried conical flasks and then 50 cm^3 of solvent were added. The testing samples were shaken for 90 s and then were left for 15 min for decantation. After adsorbent and extraction solvent were separated (during 15 min), 25 cm^3 of extraction solvent were drawn with pipette from each sample and the obtained volume of 125 cm^3 was poured into the flask marked by no. 1. Alcohol (25 cm^3) was poured into the flasks containing testing samples and the operations described above were repeated. By this method, the successive extraction solvent volumes of 125 cm^3 were obtained in flasks nos. 2, 3, 4 and 5. After 15 min lasting second decantation of adsorbent trace amounts, the samples (25 cm^3) were drawn and placed on glass pans marked by 1, 2, etc., respectively. The glass pans were put into a drier at temperature of 35°C in the aim to evaporate the solvent and to dry to constant mass.

The pans were weighed together with their contents and then after removing the fat. The mass of the respective extract contained in 25 cm^3 of extraction solvent was determined and the amount of base contained in this volume was subtracted. The obtained difference of masses m_N (N = 1, 2, 3, 4, 5) was applied to determine the efficiency of fat waste extraction from bleaching earth in the successive stages of the process.

Extractive properties of ethyl alcohol were determined by the method described above. Because we disposed of alcohol containing sodium hydroxide in amount of 0.165 mole/l, we have carried out the experiments using this reagent. Then, in the aim to check an effect of base addition on extraction, we have carried out the experiment with ethanol containing 0.323 and 0.415 mole NaOH/l. Extraction with individual NaOH solutions was performed at temperatures of 35, 50 and 65°C. Moreover, extraction with isopropyl and n-butyl alcohols was carried out under the same conditions. The process was tested using both pure alcohols and their solutions with KOH in concentrations of 0.015 and 0.118 mole/l. The potassium soaps are characterized by lower Krafft's point [11] and therefore their adsorption on bleaching earth is difficult.

Since lye is sparingly soluble in isopropyl and butyl alcohols, we used it at concentrations of 0.118 mole/l i.e. slightly lower than in case of ethanol (0.165 mole/l).

RESULTS AND DISCUSSION

In the investigation the following denotations have been used:

- N - number of process stage (successive extract N = 1, 2, 3, 4, 5);
- m_N - mass of fatty substance contained in 25 cm^3 of respective extract;
- M_N - total mass of fatty substance extracted in stages from 1 to N ($m_1 + m_2 + ... + m_N$);

Studies on extraction at the determined parameters was denominated as a series and chronologically tested series were numbered by Roman digits.

To facilitate the comparison, the obtained results are presented in Fig.1 in the form of two types of functions:

- $m_N=f(N)$; with determined trend line and correlation coefficient:
  $m_N=a\ e^b$ (1)
- $M_N=F(N)$; with determined trend line and correlation coefficient:
  $M_N=A\ LnN+B$ (2)

Where: A, B, a, b - coefficients of trend lines determined for successive data series.

The decreasing exponential function is obvious since it results from the fact that quantity of fatty substance extracted in successive stages m_N is proportional to that contained in the extracted bed. In the aim to compare the effectiveness of fatty substance extraction from oiled bleaching earth using ethyl, isopropyl and butyl alcohols, the mathematical apprehension was accepted on the basis of the obtained accurate approximation (Fig. 1) as follows:

If :

$$q = \frac{m_N}{m_{N-1}} = \exp(-b) \tag{3}$$

the successive m_N values give form the geometric convergent series:

$$m_N = m_1 q^{N-1} \tag{4}$$

however, M_N value is expressed by formula:

$$M_N = m_1 \sum_{N=1}^{\infty} q^{N-1} \tag{5}$$

Moreover, the total mass of the substance contained in the bed and extracted in successive stages of process $M_¥$ is expressed by formula:

$$M_\infty = \frac{B}{1-\exp(-b)} \tag{6}$$

The degree of bed extraction in respective stages of process is expressed by the formula:

$$a_N = \frac{M_N}{M_\infty} \tag{7}$$

where: α_N stands for degree of conversion in respective stage of process.

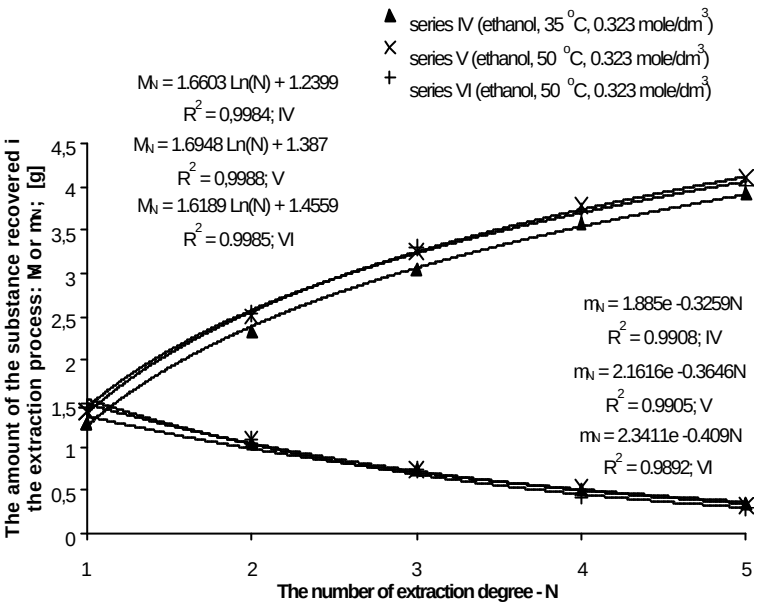

Fig. 1. Dependence of m_N, M_N on the number of degrees – N, for ethanol solution of 0,323 mole/dm^3 NaOH, m_N – amount of extract recovered in successive degree of extraction, M_N – total amount of substance recovered after N – degrees of extraction. In the aim to facilitate the comparison, the recovered results are presented in the form of two types of functions:

- $m_N = f(N)$; with determined trend line and correlation coefficient: $m_N = a\ e^{-bN}; R^2$
- $M_N = F(N)$; with determined trend line and correlation coefficient: $M_N = ALn(N) + B; R^2$

On the basis of values a, b, A, B, the degrees of conversion for the individual stages of process were calculated in order to determine the effectiveness of extraction. The value $M_\infty = 4.194\,g$ was accepted in our calculations. It is a mean arithmetic value of M_∞ for ethanolic extraction solvent, which caused dissolution of total waste substance adsorbed on bed (about 40 % of used bleaching earth). Accepting of this value allowed us to compare the effectiveness of adsorbent purification by individual extraction solvents. The experimental degrees of conversion were refereed to $\alpha_{N\max}$ value i.e. calculated theoretical degree of conversion for individual stages of process (performed according to the accepted methods) under assumption that the total adsorbed substance passed into solution in the first stage:

$$a_{N\max} = 1 - \frac{1}{2^N} \tag{8}$$

The yield W_N was recovered by dividing α_N by $\alpha_{N\max}$. It allowed us to evaluate the course of process by comparing it to the course of the most effective process:

$$W_N = \frac{a_N}{a_{N\max}} \tag{9}$$

The W_N values for the successive steps of extraction are presented in Table 1.

The results shown that the best yield of extraction was recovered in the case when ethanolic solution of sodium hydroxide in concentration of 0.323 mole/l was applied as the extraction solvent (Fig. 2). It should be noticed that the fats orecovered by using the ethanolic solution of potassium hydroxide were dark while the adsorbent recovered its initial color.

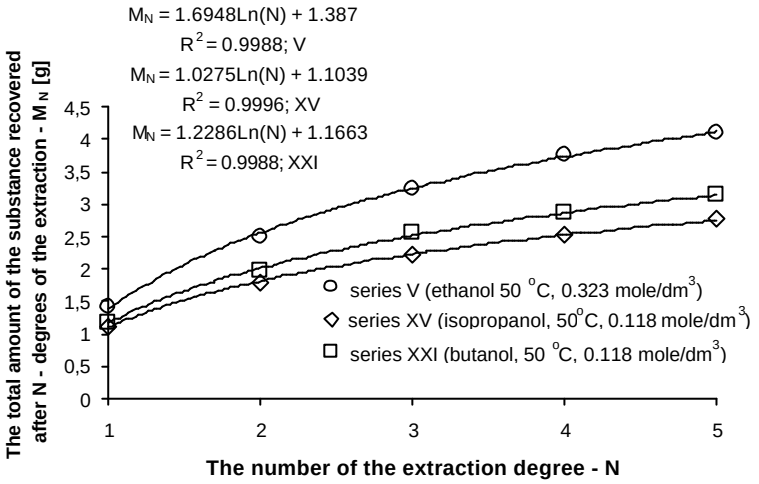

Fig. 2. Dependence of M_N on the number of degrees N for ethanol solution of 0,323 mole/dm^3 NaOH and isopropanol, butanol solutions of 0,118 mole/dm^3 KOH , M_N – total amount of substance obtained after N – degrees of extraction.

The extractive properties of isopropanol and butanol were similar but considerably worse than those of ethanolic solutions of base. This confirms an assumption that low - molecular organic solvents are not able (at temperatures applied and accepted voluminal ratio adsorbent - solvent) to extract the adsorbed substances from microporous structures for the reason of high oleophility of adsorbent. Therefore, extraction with these solvents in five stages of process involved the intergrain and microporous structures.

A low content of base in solvent have no effect on increase of the extraction effectiveness (isopropanol, butanol). It results from the insufficiently high concentration of soap in adsorptive layer.

Ethanol solution containing 0.415 mole NaOH/l made the yield worse in comparison with that containing 0.323 mole NaOH/l. One of the possible explanations of this phenomenon can be the adsorption of soaps (formed at this concentration of base) from solution.

Tab. 1. Results of calculations of W_N yield for five realized stages of process. The yield W_N (eq. 9) was obtained by dividing α_N (eq. 7) by $\alpha_{N\,max}$ (eq. 8); where: α_N stands for degree of conversion in respective stage of process, $\alpha_{N\,max}$ value i.e. calculated theoretical degree of conversion for individual stages of process.

Alcohol solution mixture	Temp. [°C]	No.of series	W_1 [%]	W_2 [%]	W_3 [%]	W_4 [%]	W_5 [%]
ETHANOL; 0.165 mol NaOH/l	35	I	41.3	55.2	61.2	66.3	71.1
	50	II	48.6	62.7	68.9	74.4	79.5
	65	III	51.6	63.5	69.1	74.1	79.0
ETHANOL; 0.323 mol NaOH/l	35	IV	59.1	76.0	83.5	90.0	96.3
	50	V	66.1	81.4	88.5	95.0	100.0
	65	VI	69.4	82.0	88.1	94.1	100.0
ETHANOL; 0.415 mol NaOH/l	35	VII	57.9	70.8	76.8	82.4	87.8
	50	VIII	64.4	76.5	82.4	88.1	93.6
	65	IX	63.6	76.1	82.1	87.8	93.4
ISOPROPANOL	35	X	43.1	50.1	53.7	57.3	60.8
	50	XI	44.8	51.7	55.2	58.9	62.4
	65	XII	47.8	53.6	56.9	60.3	63.8
ISP.; 0.015 mol KOH/l	35	XIII	44.9	51.2	54.5	57.9	61.3
ISP.; 0.118 mol KOH/l	35	XIV	50.7	55.8	58.8	62.2	65.6
	50	XV	52.6	57.7	60.8	64.3	67.9
BUTANOL	35	XVI	45.2	51.6	55.0	58.5	61.9
	50	XVII	54.7	57.8	60.3	63.4	66.6
	65	XVIII	56.1	58.9	61.2	64.2	67.5
BUT.; 0.015 mol KOH/l	35	XIX	43.7	50.5	54.0	57.5	60.9
BUT.; 0.118 mol KOH/l	35	XX	53.6	62.5	67.0	71.3	75.7
	50	XXI	55.6	64.2	68.6	73.0	77.4

The temperature increase from 35°C to 50°C improved the process yield in significantly higher degree than the increase from 50°C to 65°C for each alcoholic solution of base. It can be explained by the fact that the soaps formed in the process after reaching Krafft's point (i.e. temperature of soap transition from crystalline to amorphous state) are more easily soluble in alcohol.

CONCLUSIONS

The best properties from all the applied solvents were observed in ethanolic solution of sodium base. Optimum process conditions were achieved while applying 0.323 mole NaOH/l of ethanol. In all the realized stages of process, W_N value was the highest one for this concentration of base; in the fifth stage the adsorbed substance was totally extracted and W_1 reached the values: 59.1 % (35°C); 66.1 % (50°C); 69.4 % (65°C). It means that in the first stage, 60 % of extracted substance was in solution at temperature of 35°C and at higher temperatures the value increased to about 70 %. The yield of purification was 90 % in the forth stage under those conditions.

The action of the described alcohols is various both with respect to effectiveness and selectivity. However, application of isopropanol and butanol as solvents allowed us to obtain a transparent, slightly yellow and odourless substance. Therefore, the applied extraction solvent can be accepted as optimal depending on the aim of bleaching earth treatment. Accurate treatment of bleaching earth can be achieved by application of ethanolic solution of sodium hydroxide (the bed after drying was a loose powder having the colour characteristic for pure adsorbent). However, if the aim of treatment is fat recovery, then isopropanol or butanol solvents will be more advantageous.

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