Adsorption of Sulfur Dioxide from Water Solutions Using Hypercrosslinked Polymers

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The adsorption of sulfur dioxide from water solutions represents an important means to protect the pollution of natural lakes and soils. The main adsorbent, having a big adsorption capacity, is active carbon whose inner surface area is amounting 1000- 1200 m^2/g. Unfortunately the regeneration conditions of active carbon determine the diminution of adsorption activity and of the number of regeneration cycles. These disadvantages can be avoided using polymeric sorbents represented by hipercrosslinked polystyrene materials (macronets). Adsorbents of this kind are quite rigid, possess large transport macropores and highly developed microporous structure, ensuring both adsorption and desorption performances.

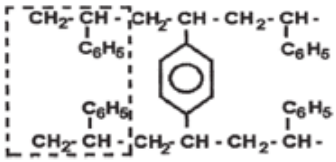
Keywords: adsorption of sulfur dioxide, hipercrosslinked polymers, macronets

Sulfur dioxide emitted from industrial plants affects the environment, polluting the lakes, poisoning flora and the living beings [1, 2]. The concentration of sulfur dioxide in residual gases attains big values (1-2 %) like in metallurgical plants. In this case the sulfur dioxide can be absorbed in industrial waters, representing a dangerous source of pollution [3]

The mentioned disadvantages can be avoided using hypercrosslinked polystyrene adsorbents known in literature as macronets (MN). Adsorbents of this kind are quite regid, possess large transport macropores and highly developed microporous structure, ensuring both adsorption and desorption performances [4-6].

The hypercrosslinked polystyrene polymers are obtained by extensive crosslinking of linear polystyrene chains. The crosslinking could be done using a bi-functional reagent as mono-chlordimetyl ether (CH_3-O-CH_2-Cl) [7].

The mono-chlor-dimetyl ether is capable of forming rigid bridges, with a very restricted conformational mobility. The crosslinking of phenol groups occurs in the presence of a Friedel- Crafts catalyst ($SnCl_4$, $TiCl_4$) using as reaction media an organic solvent as ethylene dichloride ($C_2H_2Cl_2$) in order to ensure the ultimate polystyrene swelling. Results a high crosslinked network filled with organic solvent according the scheme [8]:



The hypercrosslinked polystyrene network is characterized by a very low packing density of polymer chains in space, due to the number of rigid spacers (-CH_2). That is why the free volume of the hypercrosslinked polystyrene is high, developping a high inner surface which makes the polymeric phase accessible to small sorbate molecules [9].

The polystyrene matrix of macronet (MN) sorbents being hydrophobic will readily adsorb non-polar hydrophobic impurities. In order to ensure the adsorption of polar or ionizable molecules, the addition of hydrophilic ion exchange functional groups to the matrix must be done [10]. These functional groups can be acidic or aminic ones [11, 12].

Experimental part

For sulfur dioxide adsorption from aqueous solutions the hypercrosslinked neutral polymer MN-200 and its sulphoneted MN – 500 and aminated MN -150 derivatives had been used [13-16]. The sulphonic and aminic derivatives have been used in order to ensure the adsorption of polar ionizable molecules taking into account that in aqueous solution the following equilibrium is established:

$$SO_2 + H_2O \xleftrightarrow{K_1} H_2SO_3 \xleftrightarrow{K_2} H^+ + HSO_3^- \leftrightarrow$$
$$\xleftrightarrow{K_3} H^+ + SO_3^{2-}$$

where K_1, K_2 and K_3 represent the equilibrium constants.

In order to evaluate the adsorption efficiency of the macronets an active carbon (AC) has been used because his adsorption characteristics for gases are the best in comparison with all known adsorbents [17-22]

The main structural properties of the adsorbents used are presented in table 1. The specific area has been determined using a porosimeter Carlo Erba Sorpty 1750.

The adsorption experiments were performed using a method based on the determination of the solute concentration before and after contact with the adsorbent.

A measured volume (V= 50 mL) of sulfur-dioxide solution was placed in 250 mL vessel containing 1 g adsorbent. The initial concentration (C_0) of the solution was ranged between 3.2 and 30 g/L. The bottles were placed on a mechanical stirrer and maintained at a constant temperature. After the equilibrium was attained (24 h) the solid phase was filtered and the concentration of solution was measured. Knowing the initial and final concentration of solution, the adsorbed quantity (a) of sulfur dioxide was determined.

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Properties	MN – 200	MN -500	MNPC -150
Cumulative volume, mm^3/g	1270	605	695
Specific area, (BET), m^2/g	1090	415	442
Global porosity, %	59	51	53
Density, g/cm^3	1130	1570	1420

Table 1
THE MAIN STRUCTURAL CHARACTERISTICS OF MACRONET ADSORBENTS

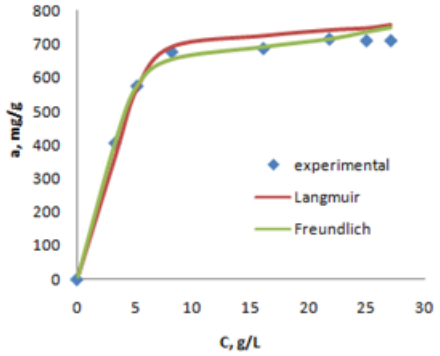

Fig. 1. The adsorption isotherms of SO_2 on active carbon

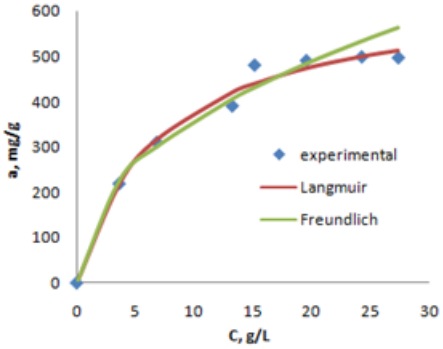

Fig. 2. The adsorption isotherms of SO_2 on MN 200

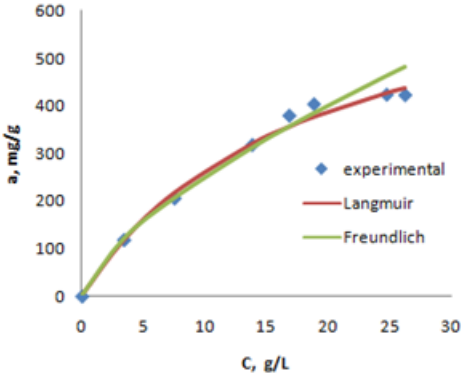

Fig. 3. The adsorption isotherms of SO_2 on MNPC 150

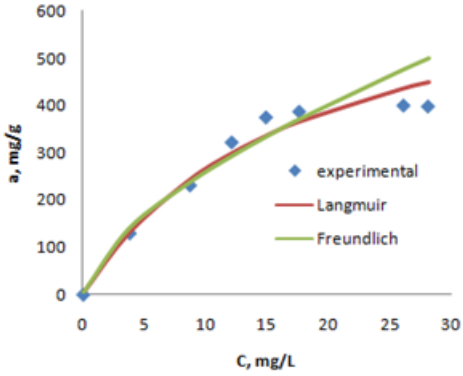

Fig. 4. The adsorption isotherms of SO_2 on MN 500

Results and discussions

In order to evaluate the adsorption capacity of the macronets MN – 200, MN – 500 and MN PC– 150 in comparison with active carbon (CA) (the last considered to be the best known adsorbent for sulfur dioxide) the adsorption isotherms have been experimentally determined (figs. 1-4).

The obtained data put in evidence that the adsorption capacity of macronets is comparable with that exhibited by active carbon. Comparing the adsorptions performances of macronets, one can see that the adsorption capacity of MN – 200 is higher in comparison with MN - 500 and MN PC – 150. The explanation consists in the presence of functional sulphonic groups – HSO_3 in MN – 500, respectively of aminic ones in MN PC – 150 (the both introduced in MN – 200 structure) as mentioned previously. These diminish considerably (from 1000 to about 400 m^2/g) the specific aria of MN – 200 modifying also another structural properties of MN – 200 (table 1).

These modifications result also from spectral characterization of the macronets, using for spectral IR domain (IR 4000-400 cm^{-1}) and UV-Vis domain (250-1859 nm) the spectrophotometer FT-IR Jasco and UV-Vis-V570 respectively. The spectral diagrams are presented in the figures 5 and 6 in coordinates Transmittance (T%) - wave number [cm^{-1}] in IR domain respectively in figures 7 and 8 in coordinates Reflectance (R%) – Wavelength (mm) in UV-Vis domain. One can see that the macronet MN – 200 presents more simple spectral lines than the macronet MN -500 and also the macronet MN PC –150 (nonfigurated).

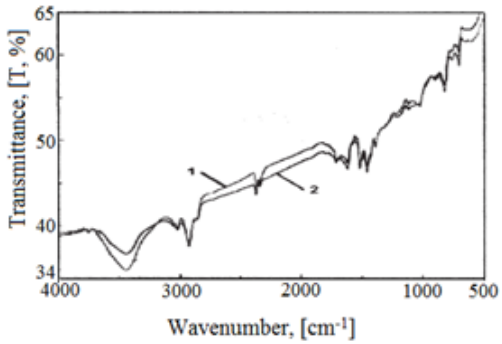

Fig. 5. Spectral diagram of macronet MN – 200 in IR domain; 1 - temperature 25°C, 2 – temperature 150°C

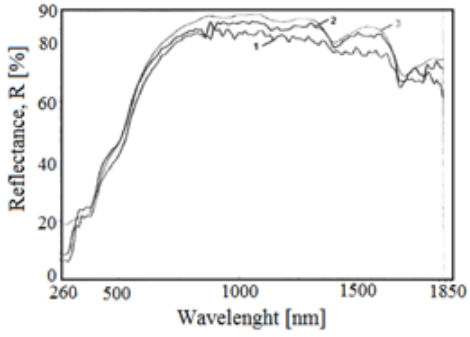

Fig. 6. Spectral diagram of macronet MN-200 in UV-Vis domain; 1 - temperature 25°C, 2- temperature 120°C, 3- temperature 150°C

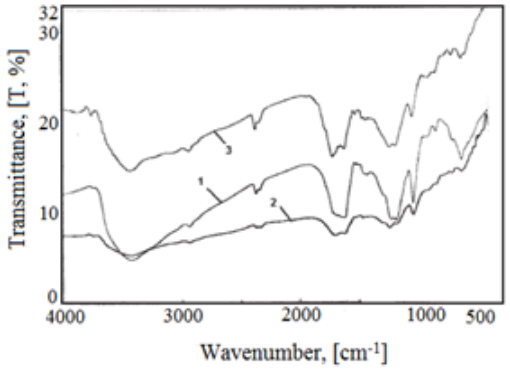

Fig. 7. Spectral diagram of macronet MN- 500 in IR domain;
1 - temperature 25°C, 2 - temperature 120°C, 3 - temperature 150°C

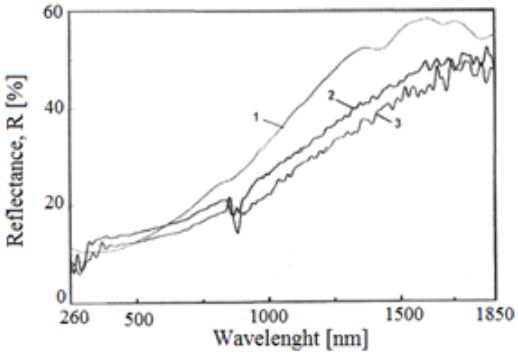

Fig. 8. Spectral dagram of macronet MN – 500 in UV-Vis domain
1 - temperature 25°C, 2- temperature 150°C

Langmuir,	R^2	Freundlich,	R^2
Active carbon	0.99254	Active carbon	0.9647
MN PC 150	0.9841	MN PC 150	0.909
MN 500	0.9954	MN 500	0.979982
MN 200	0.9848	MN 200	0.97982

Table 2
THE VALUES OF R^2 PARAMETER CHARACTERISING THE SULFUR DIOXIDE ADSORPTION ON ACTIVE CARBON AND MACRONETS

In order to put in evidence the more appropriate form of isotherms of active carbon and macronets, the adsorption isotherms Langmuir and Freundlich have been used. The Langmuir isotherm is based on a theoretical model for monolayer adsorption. The Freundlich isotherm is an empirical one, suitable for the heterogeneous surface in a restricted range of concentrations.

The Langmuir, model is described by the following equation:

$$a = a_m \cdot \frac{bc}{1 + bc} \quad (1)$$

where a represents the concentration at equilibrium, of sulfur dioxide adsorbed on solid phase, in mg/g;

a_m – the maximum concentration of sulfur dioxide adsorbed on monolayer;

b – the equilibrium constant;

c – the concentration of sulfur dioxide, at equilibrium, in liquid phase, in g/L.

Representing the Langmuir equation in linear form one obtain:

$$\frac{1}{a} = \frac{1}{a_m bc} + \frac{1}{a_m} \quad (2)$$

Making the variable changes $\frac{1}{a} = y$ and $\frac{1}{c} = x$, a linear equation results, having the form:

$$y = Ax + B \quad (3)$$

where A and B are constants.

Finally a linear regression is obtained that can be solved by the last square method.

The Freundlich equation is described by following equation:

$$a = Kc^{\frac{1}{n}} \quad (4)$$

where a represents the concentration at equilibrium, of sulfur dioxide adsorbed on solid phase, in mg/g;

c – the concentration at equilibrium, of sulfur dioxide in liquid phase, g/L;

K and n – constants.

The equation (4) can be linearized as follows:

$$\ln a = \ln K + \frac{1}{n} \ln c$$

Making the variable changes , a linear equation results, having the form:

$$y = Ax + B$$

As previously, a linear regression is obtained, solved by the last square method.

As resulted from figures 1-4 the most probable form of isotherms characterizing the adsorption process of sulfur dioxide on active carbon and macronets is the Langmuir isotherm, confirmed by the data from table 2. In all cases the values of R^2 (the quadratic value of correlation coefficients) are bigger considering the Langmuir isotherms in comparasion with the Freundlich ones.

Conclusions

In the present work, the adsorption capacity of hipercrosslinked polymers (macronets) in comparison with active carbon is analyzed. Adsorbants of this kind are quite rigid and resistant and possess large transport macropores and highly developed microporous structure. These characteristics confer to macronets a big adsorption capacity, comparable with that of active carbon, the last considered as the best adsorption material.

It must be mentioned that the regeneration conditions of active carbon determine the diminution of adsorption activity and of the number of regeneration cycles. These disadvantages are avoided using hipercrosslinked polymers more resistant, especially at mechanical solicitations.

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