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Kinetic Aspects of Methylene Blue Adsorption on Blast Furnace Sludge

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In this paper the potential of blast furnace sludge (BFS) in methylene blue (MeB) removal from aqueous solutions was studied by following the adsorption of dye. The BFS was used without any modification/activation. The kinetics of adsorption on the sludge was studied in laboratory batch experiments by monitoring the effect of contact time and dye concentration (20–160 mg L⁻¹) on the adsorption capacity at room temperature (293 K) and at natural pH (7±0.5). It was found that the adsorption capacity at equilibrium increased from 10.3 to 70.6 mg g⁻¹, as the initial MeB concentration increased from 20 to 160 mg L⁻¹.

For analysis of experimental data, three kinetic models were applied: pseudo first-order, pseudo second-order and Weber-Morris intra-particle diffusion model. Results demonstrate that kinetics of dye adsorption on BFS is best described by the pseudo second-order equation ($R^2 \geq 0.99$, $F\text{-value}=0.86$) while fitting to Weber-Morris model has shown that the pore diffusion is not the only rate limiting process in MeB-uptake. Such kinetics can be related to surface characteristics of BFS used: particle diameter $d_p \leq 56$ mm, specific area 31.46 m² g⁻¹, pore volume $157 \cdot 10^{-3}$ cm³ g⁻¹, and average pore diameter 17.88 nm, mark this industrial by-product as a mesoporous material. Its surface morphology change after MeB adsorption was confirmed by SEM/EDS analyses.

The results obtained allow concluding that untreated BFS has the capacity for MeB uptake within the range of concentrations employed and could be considered as potential low cost adsorbent for treating of dye-polluted waste waters.

Key words:

industrial waste, blast furnace sludge, Methylene Blue, batch adsorption

Introduction

In the global steel industry, more than 400 kg of solid byproduct is generated per ton of steel produced. Most of this by-product (70–80 %) is in the form of slag, which is used largely in the cement industry and for road and civil construction. The remaining solid by-products can be classified as dusts, sludge and oily/non-oily mill scale. Traditionally, the majority of generated dust, sludge and scale are recycled back to the blast furnace by means of the sintering process. The fraction of solid by-products classified as “fine particles” (60 % of dusts and sludge) is very difficult to recycle without extensive pre-treatment and until recently, it has been deposited in landfills. These by-products are problematic to recycle not only because of their small particle size, but also for their high content of impurities, of which the saleable content is not high enough to make further processing economical¹. In recent years the costs for depositing in landfills have increased due to lack of space and due to increasing environmental restrictions. years, the costs for de-

positing in landfills have increased due to lack of space and increasing environmental restrictions. The latest regulations have changed the industry's perception of the problems related to hazardous by-products. The combination of toxicity and reactivity, as well as the quantity of released compounds may lead to serious pollution of the natural environment. Environmental concerns have also increased over the years from a global viewpoint, especially in the regions with thermo-power energy pollution, vehicular traffic and heavy industries that release chemical effluents. Current policies at regional and national levels necessarily lead to an increase in efforts for purification of surface water, ground water, and industrial or household wastewater that contains many different types of pollutants. These pollutants include inorganic and organic compounds and are more or less hazardous to humans, animals and plants.

Dyes are important pollutants in wastewater, which are mainly discharged from textile, printing, food and leather industries². Various types of dyes including basic, acidic, reactive, and dispersive dyes are widely used. Dyes in waters affect the nature of the water, inhibiting sunlight penetration

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into the stream and reducing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic. Removal of these contaminants requires cost effective technologies and a variety of techniques have been developed in the past decades in dealing with wastewater treatment.

Adsorption is a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent. These can be natural materials, by-products or industrial wastes, or those requiring less energy and time to be produced. Activated carbon³, clay minerals^{4,5}, biomaterials⁶, zeolites⁷, and some industrial solid wastes^{8,9} have been widely used as adsorbents for adsorption of organics and ions¹⁰ in wastewater treatment. The advantage of using industrial by-products lies in the fact that these materials can be converted either into useful adsorbents or potential resources of secondary materials^{11,12}.

In this paper, the research in cationic dye (Methylene Blue, MeB) uptake using industrial waste (Blast Furnace Sludge, BFS) as potential adsorbent in polluted water treatment will be presented. The focus of the research was to evaluate the adsorption potential of BFS for methylene blue, having in mind the fact that BFS is an inexpensive and affordable material.

Methylene blue was chosen in this study because of its strong adsorption onto solids. It also has often served as a model compound for removing organic contaminants and colored pollutants from aqueous solutions^{13–17}.

In order to test the application of BFS in textile wastewater treatment, the kinetic data on adsorption studies were analyzed with the aim to understand the adsorption mechanism of the dye molecules onto the BFS.

Experimental

Methylene blue

MeB is the most commonly used material for dyeing cotton, wood, and silk. The chemical structure of the dye is shown in Figure 1. MeB supplied by J.T. Baker (analytical grade, chemical formula $C_{16}H_{18}ClN_3S$, $M = 319.87 \text{ g mol}^{-1}$) was used as an adsorbate, without prior purification. All working

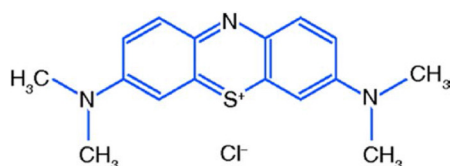


Fig. 1 – Chemical structure of cationic dye Methylene Blue

solutions were prepared from MeB stock solution (10^3 mg L^{-1}) diluted with distilled water. In aqueous solutions, MeB is a cationic dye, $C_{16}H_{18}ClN_3S^+$.

Blast furnace sludge

The original blast furnace sludge was collected in Sisak, Croatia. The wet sample was dried at $105 \text{ }^\circ\text{C}$ for 4 h, then subsequently ground and sieved to yield a powder of a particle diameter, $d_p \leq 56 \text{ } \mu\text{m}$. Different methods were used for characterization of BFS¹⁰: Chemical characterization was done by PIXE, conventional X-ray diffraction analysis (by Rietveld refinement) yields a qualitative mineralogical composition and the surface area properties were determined by the Brunauer-Emmett-Teller (BET) method using N_2 adsorption-desorption isotherms. SEM/EDS analyses were performed with scanning electron microscope Tescan Vega LSH (Czech Republic) equipped with “Bruker” EDS spectrometer.

Batch equilibrium studies

Laboratory batch adsorption experiments were carried out in order to follow adsorption kinetics of cationic dye on blast furnace sludge. Adsorption has the advantage of easy operation, low energy consumption, simple maintenance and large capacity. Experiments were performed in a set of PET flasks (100 mL). Solutions of dye (20 mL) with different initial concentrations ($10\text{--}200 \text{ mg L}^{-1}$) were prepared from the stock solution ($C = 10^3 \text{ mg L}^{-1}$). An equal mass of 0.03 g BFS of particle size $\leq 56 \text{ } \mu\text{m}$ was added to dye solutions and kept in shaker at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$) for 30 min. The flasks were then removed from the shaker and left for 4.5 h to reach equilibrium of the solid-solution mixture (revealed by preliminary experiments), when the final concentration of dye in the solution was analyzed. A similar procedure was followed for another set of flasks containing the same dye concentration without BFS to be used as a blank. Experiments were performed at the natural pH (7.0 ± 0.5), which was not significantly changed after the system had reached equilibrium. The amount of MeB per unit of adsorbent at equilibrium ($q_e, \text{ mg g}^{-1}$) was calculated by using Equation (1):

$$q_e = V(C_o - C_e) / m \quad (1)$$

where C_o and C_e (mg L^{-1}) represent concentrations of dye at initial time, and at equilibrium in the solution, respectively. V is the volume of solution (L), and m is the mass of dry adsorbent used (g).

The concentration of methylene blue in the supernatant solution before and after adsorption was determined using Perkin Elmer Coleman 54 spectrophotometer at $\lambda = 665 \text{ nm}$.

Prior to the kinetic measurement, a calibration curve was obtained by using the standard MeB solution with known concentrations. It was found that the calibration curve was very reproducible and linear over the concentration range used in this work.

Batch kinetic studies

The procedures of kinetic experiments were identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of MeB were similarly measured. The amount of adsorption at time t (q_t , mg g^{-1}) was calculated by Equation (2):

$$q_t = V(C_o - C_t) / m \quad (2)$$

where C_t (mg L^{-1}) represents concentrations of dye at any time t , and the other symbols are the same as in Equation (1).

The adsorption kinetics of the MB on BFS was tested at different initial concentrations. Three measurements were made for each sample and the results were averaged. The confidence of experimental data was checked by calculating the standard deviation and applying the “ 3σ criterion” for the rejection of data outside the confidence interval.

Results and discussion

Adsorption equilibrium – Effect of contact time and initial concentration

Adsorption equilibrium can be described as a state of dynamic equilibrium, where both adsorption and desorption rates are equal. Such a state is established when the concentration of dye in the bulk solution is in dynamic balance with that on the surface, depending on different experimental conditions. The effect of initial dye concentration and contact time on the adsorption rate of MeB by BFS is illustrated in Figure 2.

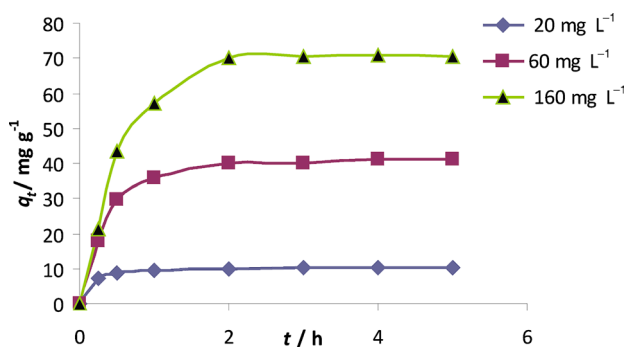


Fig. 2 – Effect of contact time and initial dye concentration on adsorption of MeB onto BFS from aqueous solutions at 293 K

As shown, the removal of dye increases with increasing initial dye concentration. Also, it appears that a rapid initial adsorption occurs, with equilibrium reached in 120 min. The adsorption capacity at equilibrium, q_e , increased from 10.3 and 41.2 to 70.6 mg g^{-1} , as the initial MeB concentration increased from 20 and 60 to 160 mg L^{-1} .

The rate of adsorption for the three initial concentrations shown in Figure 2 has a feature common to all the other initial MeB concentrations studied in this work: The removal of dye by adsorption on BFS was found to be rapid at the initial period of contact time and then to slow down with time. The fast uptake of MeB molecules in the first 30 minutes of the contact suggests that dye transfer through the bulk solution plays the major role at this stage of the process. This can be explained by the attractive forces between the dye molecule and the adsorbent (such as Van der Waals forces and electrostatic attractions) with negligible interference from MeB-MeB interactions. Furthermore, the fast diffusion of MeB onto the external surface of BFS is followed by slower adsorption steps, depending on the surface sites left unoccupied by the dye.

Adsorption kinetics

Adsorption kinetics is one of the most important characteristics representing the adsorption efficiency. In the present paper, three kinetic models were applied to adsorption kinetic data in order to investigate the adsorption process of MeB dye onto BFS. These models include the pseudo first-order, pseudo second-order, and the intra-particle diffusion equations. In regression analyses performed, R^2 value indicates that the model successfully describes the kinetics of adsorption.

The pseudo first-order kinetic model

The pseudo first-order kinetic model has been widely used to predict dye adsorption kinetics. A linear form of pseudo first-order model was described by Lagergren [18], Equation (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t is the amount adsorbed at time t (mg g^{-1}), and k_1 (h^{-1}) is the rate constant of pseudo first-order adsorption.

Using Equation (3) and values in Figure 2, $\ln(q_e - q_t)$ versus t was plotted at different MeB concentrations, as shown in Figure 3. This plot gives the value of the constant k_1 and also q_e (mg g^{-1}) can be calculated. If the first-order kinetics is applicable, then the plot should show a linear relationship.

The plot $\ln(q_e - q_t) = f(t)$ gave the linear correlation for the lowest MeB concentration ($C_o = 20 \text{ mg L}^{-1}$) only. The calculated Lagergren first-or-

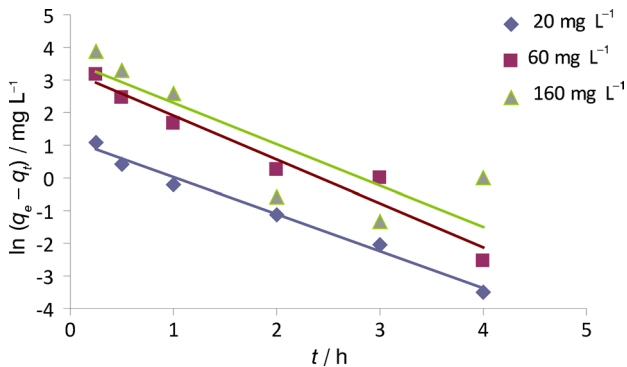


Fig. 3 – Pseudo first-order kinetics for adsorption of MeB onto BFS at 293 K

der rate constants k_1 determined from the plot are presented in Table 1 along with the corresponding linear regression correlation coefficients R^2 . It has to be noticed that the rate constant k_1 firstly increased with an increase in initial concentration, and then decreased. This shows no applicability of the pseudo first-order model in predicting the kinetics of the MeB adsorption onto BFS particles. The correlation coefficients R^2 which are lower for the increased concentrations, also confirm this.

The pseudo second-order kinetic model

The kinetic data were further analyzed using pseudo second-order kinetics, represented by Ho and McKay¹⁹, Equation (4):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where k_2 is the rate constant of second-order adsorption, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of methylene blue adsorbed at equilibrium and at time t . A plot between t/q_t versus t gives the value of the constant k_2 ($\text{g mg}^{-1} \text{h}^{-1}$). If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. The curves $t/q_t = f(t)$ are given in Figure 4.

The plots of t/q_t versus t show linear correlation for all initial concentrations of MeB. The applica-

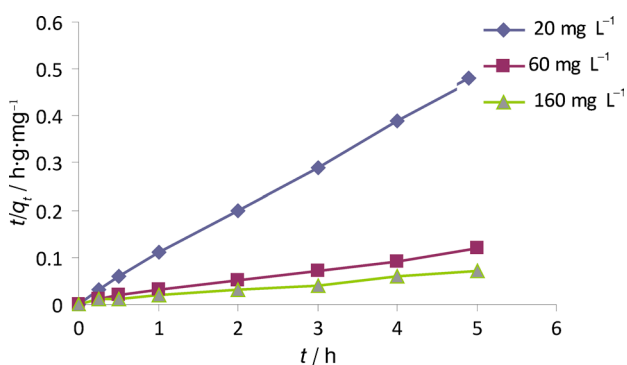


Fig. 4 – Pseudo second-order kinetics for adsorption of MeB onto BFS at 293 K

bility of pseudo second-order equation to describe the adsorption process was judged based on the correlation coefficients (R^2), which are a measure of goodness of fit. Pseudo second-order rate constants k_2 (calculated from the intercept and slope) as well as linear regression correlation coefficients R^2 are summarized in Table 1. The results show that correlation coefficients R^2 for the pseudo second-order kinetics are greater than those for pseudo first-order, indicating good agreement with the experimental data. It can be inferred that the pseudo second-order equation fits the adsorption data better than the pseudo first-order model. The fitness of this model was further verified by using F -test as statistical tool for error estimation, in order to evaluate whether the model is adequate to describe the experimental data²⁰. The higher R^2 and F -values are better for data fitness.

Table 1 – Kinetic parameters for the adsorption of cationic dye MeB on BF sludge at 293 K

	Initial concentration of MeB, $C_0 / \text{mg L}^{-1}$		
	20	60	160
Experimental $q_e, \text{mg g}^{-1}$	10.33	41.18	70.56
Pseudo first-order model			
k_1 / h^{-1}	1.13	1.34	1.27
$q_{e\text{-calc}}, \text{mg g}^{-1}$	3.116	26.869	36.191
R^2	0.9981	0.9569	0.7269
F -value	0.7950	0.8110	0.3149
Pseudo second-order			
$k_2 / \text{g mg}^{-1} \text{h}^{-1}$	0.775	0.0738	0.0331
$q_{e\text{-calc}}, \text{mg g}^{-1}$	10.64	45.66	76.92
R^2	0.9996	0.9947	0.9895
F -value	0.8592	0.9948	0.6766

On the basis of given R^2 and F -values in Table 1, it can be confirmed that the pseudo second-order model has the best goodness of fit among the applied equations.

However, these two kinetic models fitted are not able to identify all the steps involved in the adsorption process because the adsorption kinetics is controlled by different steps: Solute transfer to the adsorbent particle surface through a boundary layer, adsorption on the particle surface and transfer from the particle surface to the intra-particle active sites. Therefore, contribution of intra-particle diffusion mechanism to complex mechanism of MeB interaction with BFS was also tested.

Intra-particle diffusion model

During the adsorption experiments in batch reactors, the spontaneous diffusion and stirring provide the transport of MeB molecules from the bulk into the pores of the adsorbent, as well as adsorption at the outer surface of the adsorbent. The rate-limiting step may be either film diffusion or intra-particle diffusion. As they act in series, the slower of the two will be the rate determining step. The possibility of MeB to diffuse into the interior sites of the BFS-particles was tested with Weber-Morris equation, known as intra-particle diffusion model^{21,22}. It includes an empirical function relationship common to most adsorption processes in which the quantity of adsorbed substance varies almost proportionally with $t^{1/2}$ according to the following Equation (5):

$$q_t = k_{int} t^{1/2} + I \quad (5)$$

where k_{int} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{h}^{-0.5}$), q_t (mg g^{-1}) is the amount of dye adsorbed at time t (h). A plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{int} and intercept I . Values of intercept give an idea about the thickness of the boundary layer: The larger the intercept the greater the boundary layer effect. If the plot passes through the origin, then the rate limiting process is only the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved^{23,24}. Figure 5 shows plots of mass of dye adsorbed, q_t versus $t^{1/2}$ for the system under study.

The results of experiment indicate that the adsorption process exhibits two separate regions with two straight lines. Multilinearity in Figure 5 and deviation of the straight lines from the origin suggest that intra-particle diffusion was not the only rate limiting mechanism in the adsorption process. Such behavior may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption²¹. This is confirmed by the values of the

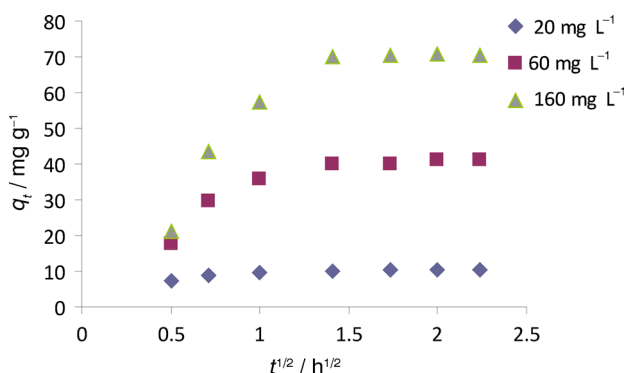


Fig. 5 – Intra-particle diffusion plots for MeB onto BFS at 293 K

intra-particle diffusion constants k_{int-1} and k_{int-2} (calculated from two linear approximations of Weber – Morris plots) presented in Table 2 along with the corresponding regression coefficients R^2 .

Table 2 – Kinetic parameters for intraparticle diffusion of cationic dye MeB during the adsorption on BF sludge at 293 K

	Initial concentration of MeB, $C_0 / \text{mg L}^{-1}$		
	20	60	160
Experimental q_e , mg g^{-1}	10.33	41.18	70.56
Intra-particle diffusion model			
$k_{int-1} / \text{mg g}^{-1} \text{h}^{-0.5}$	4.09	35.08	70.73
R^2	0.9224	0.9257	0.9520
$k_{int-2} / \text{mg g}^{-1} \text{h}^{-0.5}$	0.400	1.724	0.7720
R^2	0.9283	0.9082	0.7994

The high k_{int-1} values and the related R^2 coefficients indicate that the first stage of intra-particle diffusion is faster than the second stage, which is also visible in Figure 5. The first straight part of the plots can be attributed to a macropore diffusion process while the second linear portion reflects the micropore diffusion process and may be correlated with the very slow diffusion of the adsorbed MeB from the surface film into the micropores, which are the least accessible sites for adsorption. More insight into such considerations can be obtained from surface area characteristics of BFS, as presented in the next section.

Surface area properties of BF sludge

The surface area properties were determined by BET, while SEM was used to study the morphological features and surface characteristics of the adsorbent material before and after the contact with MeB.

BET surface area of BFS in the present study has the value $S_p = 31.46 \text{ m}^2 \text{ g}^{-1}$, total pore volume (1.7–300 nm) is $V_p = 157 \cdot 10^{-3} \text{ cm}^3 \text{ g}^{-1}$, and average pore diameter $d = 17.88 \text{ nm}$ ¹⁰. According to IUPAC classification²⁵ of porous solids into three groups (micropores with $d < 2 \text{ nm}$, mesopores with $2 \text{ nm} < d < 50 \text{ nm}$, and macropores with $d > 50 \text{ nm}$), BF sludge here used may be considered a mesoporous material. Such surface area properties are beneficial for its adsorbent potential and could be explained by the fine grained particle's size and their porous nature, as it was revealed by SEM images, Figure 6. Micrographs were registered in order to assess the morphological changes in the BFS surface following adsorption of MeB.

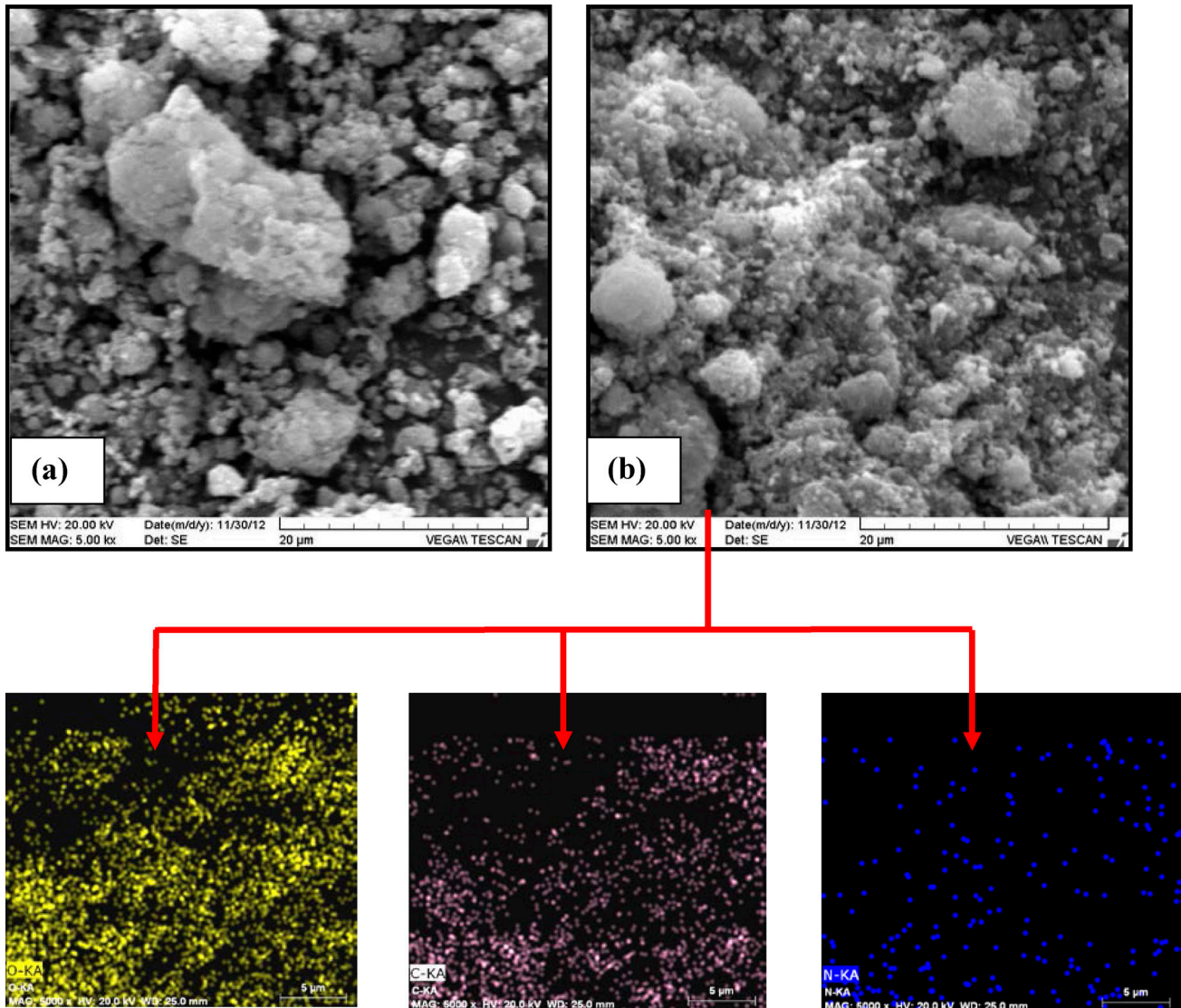


Fig. 6 – SEM micrographs of blast furnace sludge: (a) before and (b) after adsorption of MeB, showing elemental mapping for oxygen, carbon and nitrogen

As it can be seen from the topography in Figure 6a, BF sludge is a crystalline adsorbent with heterogeneous pores within the particles and inter-particles cavities. Micropores and mesopores contribute to the rough surface morphology, while the considerable number of heterogeneous crystalline particles offers the possibility for MeB to be adsorbed.

After the adsorption, the morphology of the loaded adsorbent (Figure 6b) showed a remarkable difference: BFS is characterized by a smooth surface and its structure is less porous due to reduced pore size. The presence of O, C, and N at the surface clearly witnessed that the original surface morphology of BFS had been changed due to particles covered by adsorbed MeB. Observations made by SEM reflect the complex mechanism of MeB uptake, which can be related not only to the chemistry in the solution, but also to the active sites and surface charge of

adsorbent²⁶. Namely, the surface of BFS contains a large number of active sites, depending on its mineralogical composition. As it was referred¹⁰, BFS used in this study was composed mostly of carbon and different oxides. Oxygenated surface functional groups of these constituents get negatively charged in water solutions at $pH >$ isoelectrical point: It favours the adsorption of positively charged MeB-ions from solutions^{27,28}. On the basis of experiments performed here at natural pH of MeB solutions (pH 7 at 293 K), it can be inferred that dye –cations were attracted to the negatively charged functional groups at BFS surface. Therefore, formation of MeB – layer over the BFS surface can be presented by the following equations:



Kinetic aspects of MeB adsorption here outlined are comparable with contributions of other studies devoted to non-conventional adsorbents for dye removal^{29,30}. The comparison with the results using similar adsorbent (treated BFS) and same adsorbate, reconfirmed those obtained formerly³¹. Even more, the natural BFS here used has the comparative advantage if adsorption capacity q_e (mg g^{-1}) serves as the basis of comparison: 6.4 mg g^{-1} was reported for treated BFS³² having the specific surface $28 \text{ m}^2 \text{ g}^{-1}$, while q_e of 70.6 mg g^{-1} was measured here for the non-treated one with BET-surface of $31.46 \text{ m}^2 \text{ g}^{-1}$.

It is also worth to mention that a literature survey of more than 180 recently published articles on MeB adsorption has shown the strong scientific progress in this subject³³. However, the lack of commercialization is still evident due to significant financial and technological efforts connected to a scale up from laboratory to industry. Taking that into consideration, the contribution of present paper is the approach where a non-treated BF sludge is used, which would make its application even cheaper.

The feasibility of using metallurgical “waste” BFS as a low cost adsorbent for MeB was in the focus of this study. Results have shown that the utilization of such by-product if used as adsorbent cannot only minimize its disposal cost, but can also remove cationic dyes from aqueous solutions.

Conclusions

– In this study, the effectiveness of blast furnace sludge (BFS) in methylene blue (MeB) removal from aqueous solutions was evaluated by laboratory batch experiments.

– The yield of adsorption increased with increasing the initial concentration of MeB.

– Kinetics of MeB adsorption on BFS follows the pseudo second-order kinetic model.

– The intra-particle diffusion results revealed the importance of macropores in the first stage of the adsorption process, while diffusion in micropores dominated in a second slow stage.

– BFS displayed remarkable performance towards removal of MeB from aqueous solution, showing a maximum adsorption capacity of 70.6 mg g^{-1} .

– The results suggest that BFS, a by-product of the iron making industry, has the potential to be converted into a value-added product useful in solving both the problem of industrial waste disposal and industrial wastewater treatment.

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