
Flexible PVC-Silica Composites as an Adsorptive Material for Water Soluble Dyes

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SUMMARY

Methylene Blue (MB) adsorption studies were performed on flexible Polyvinyl Chloride/Silica composites which were obtained by using plastisol-plastigel technology. Change of MB concentration in aqueous phase as the adsorption process advanced was followed by using visible spectroscopy. The diffusion of MB through the composites exhibited non-Fickian behavior with a diffusivity of $10^{-11} \text{ m}^2\text{s}^{-1}$. Making use of such PVC-silica composite sheets as column packing, the packing time will be reduced and the surface available for diffusion will be increased.

Keywords: PVC-silica composites, Methylene Blue, Adsorption, Water soluble dye, Methylene Blue adsorption

1. INTRODUCTION

Removal of water soluble dyes from aqueous systems using adsorption is of environmental importance. Basic dyes and methylene blue (MB) are the most studied probe dyes for this purpose. In removal of dyes as well as pure adsorbents, composite materials having adsorbents as dispersed phase are used. Silica (SiO_2) gel, silica aerogel¹, highly ordered mesoporous silica structures², diatomaceous silica³, luffa fibers⁴, rice hull ash⁵ polyurethane foams⁶ are examples of the pure adsorbents recently used for methylene blue adsorption. Composite materials such as rice husk/silica nanocomposite⁷, activated carbon/cobalt ferrite, alginate composite beads⁸, humic acid immobilized polymer/bentonite composites⁹, polymer/activated charcoal composites¹⁰, activated carbon and conducting polymer composites¹¹,

chitosan based materials¹², acrylic amide and acrylic acid copolymer and polyvinyl alcohol interpenetrating networks¹³ are the composite materials used for this aim.

Silica gel is one of the good adsorbents for dye adsorption from water, but its colloidal dispersion in water creates turbidity. Embedding silica into a plastic matrix both improves dye absorptivity of the plastic and prevents the contamination of the aqueous phase by silica. Polyvinyl chloride (PVC) is a polymer for dispersing and encapsulating silica gel using different methods. For instance dispersion of silica in PVC could be made by dispersing it in vinyl chloride prior to suspension polymerization¹⁴. A plasticized PVC with increased porosity has been developed by the use of organic/inorganic hybrids¹⁵. Melt mixing is another method to prepare PVC/ SiO_2 nanocomposites¹⁶.

The elasticity of PVC can be controlled by adding plasticizers. Phthalate and non phthalate plasticizers could be used for preparation of flexible PVC materials. Since phthalate plasticizers have undesired health effects nonphthalate plasticizers are preferred recently¹⁷.

Diocetyl phthalate (DOP) is a well known and versatile plasticizer that could be used in research for flexible PVC preparation.

Thus in the present study composites were prepared by mixing PVC powder, DOP and silica to prepare composites for dye adsorption.

The objective of the present study is to incorporate the adsorption capacity of silica into a plastic matrix so that to obtain a system which has a high capacity for dye adsorption and is convenient to use in ease for column applications¹⁸ as stacked or pelletized. Therefore, a composite material having silica incorporated into a plastic matrix composed of plasticized PVC with DOP has been produced and characterized in terms of the adsorption behavior.

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2. METHODS

2.1 Materials

Polyvinyl chloride, PVC, powder (Petvinyl P 38/74, emulsion, $63\ \mu\text{m}$, $1.39\ \text{g}/\text{cm}^3$ density, $16\ \text{m}^2/\text{g}$ specific surface area, Petkim Co., Turkey), Dioctyl phthalate (DOP, Sankim Co, Turkey), Epoxidized Soybean Oil (ESBO, Akdeniz Kimya Co, Turkey), Calcium Stearate (CaSt_2 , Merck, Germany) Zinc Stearate (ZnSt_2 , Merck), Precipitated Silica (Zeo 49, Huber Corp., USA) are used as they are, to produce composites.

2.2 Plastisol and Composite Preparation

A hundred g PVC and 60 g DOP, 5 g ESBO, 2.75 g CaSt_2 and 0.275 g ZnSt_2 were mixed and a homogeneous plastisol was obtained by stirring at 200 rpm in a laboratory type dough kneader. Small aliquots of plastisol mixed with 2, 4, 8, 12 and, 16% in mass silica powder, in a porcelain mortar with a porcelain handle. The entrapped air in the plastisol and composites were removed by means of vacuum.

2.3 Sheet Preparation

Gelation of the above plastisol at $140\pm 2\ ^\circ\text{C}$ for 16 minutes, between A316 stainless steel plates under 5 MPa pressure in a hot press led to the formation of plastic sheets of 314–560 μm thick. The sheets were taken out of the press after cooling down to $40\ ^\circ\text{C}$.

2.4 Morphological Studies

The SEM microphotographs of the gold coated PVC powder and silica were obtained with ETD technique by using Philips XL 30 S FEG and QUANTA 250F SEM instrument, respectively. SEM microphotographs of the gold coated fracture surfaces obtained immersing the sheets in liquid nitrogen were taken by using QUANTA 250F SEM instrument using both secondary electron (ETD) and backscattering electron (BSED) techniques.

2.5 Water Sorption of Composites

Strips of sheets were immersed in pure water for two weeks and they were weighed after removing them from water and blotting with tissue paper.

2.6 Adsorption Isotherm Measurement

Equilibrium uptakes from $0.018\ \text{g}\ \text{dm}^{-3}$ MB solution by PVC composites without silica and with 16% silica, PVC and silica powders were determined at $25\ ^\circ\text{C}$ measuring MB solution concentrations by using Jasco 7800 UV - Vis spectrophotometer. All MB containing solutions were kept in dark to prevent the attack of sunlight.

2.7 Adsorption Rate Experiment

On liquid side: Ten PVC composite pellets having 0–16% silica were immersed in $50\ \text{cm}^3$ $0.018\ \text{g}\ \text{dm}^{-3}$ MB solutions. $5\ \text{cm}^3$ solution and one pellet were taken out of the flask at each time, to keep the solid/liquid ratio unchanged during adsorption. MB concentration in the liquid phase was measured by means of visible spectroscopy.

On solid side: The plastigel and the composite sheets were equilibrated with $0.04\ \text{g}\ \text{dm}^{-3}$ MB solution. The visible spectra of MB adsorbed sheets were taken by using transmission technique in Perkin Elmer 3 UV- visible spectrophotometer. The microphotographs of the sheets were taken with transmission technique, using Olympus, CH40 microscope.

3. RESULTS AND DISCUSSION

Flexible PVC-silica composites, having a porous structure were produced by using plastisol-plastigel technology. While equilibrium uptake evaluations were performed through visible spectroscopy and optical microphotography studies, a kinetic study was performed for the MB adsorption of composites, as well.

3.1 PVC and Silica Powders

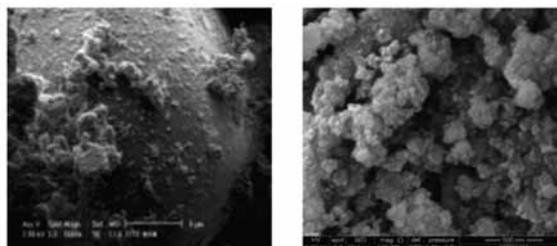
The morphologies of PVC and silica powders are seen in **Figure 1**. PVC powder has a large particle size distribution. The spherical particles had a wide range of size distribution. Silica powder particles were agglomerated and smaller in size than PVC particles. The average particle size of PVC particles was reported as $9\ \mu\text{m}$ ¹⁹.

The density, the surface area, and the pore volume of silica were $1.58\ \text{g}\ \text{cm}^{-3}$, $148\ \text{m}^2\ \text{g}^{-1}$ and, $0.12\ \text{cm}^3\ \text{g}^{-1}$, respectively.

3.2 Structure of Composites

PVC plastisols are gelled by swelling of PVC particles with the plasticizer, fusion and crosslinking of the swollen particles to each other during heating. A mesoporous silica was dispersed in plastisols by mixing before gelation process. The plastisols were gelled by heating at $140\ ^\circ\text{C}$. This temperature was chosen, since PVC was not thermally stable at higher temperatures.

Figure 1. SEM micrographs of (a) PVC powder, (b) Silica powder



The morphology of the composite films having 12 and 16% silica are shown in **Figure 2**. As seen in the Figure silica particles are embedded in continuous phase of plasticized PVC and they created a porous structure.

The density of the flexible composite sheets of 314 - 563 μm thickness, as measured by using water in a glass pycnometer, increased from 1.098 to 1.231 g/cm^3 as the silica content increased. The sheets had up to 7.3% empty volume which could be attributed incomplete air removal due to high viscosity of the plastisol. The composites absorbed 1.92 to 6.07% water from liquid water as their silica content increased²⁰.

3.3 MB Adsorption Isotherm

The adsorption isotherms of MB on silica and the composite having 16% silica are shown in **Figure 3**.

The adsorption isotherms fitted to Langmuir model shown by Equation (1).

$$1/Q = 1/Q_m + C / (Q_m K) \quad (1)$$

Where:

K = Langmuir constant ($\text{dm}^3 \text{mg}^{-1}$)

Q_e = MB concentration at equilibrium in powder (mg g^{-1})

C_e = MB concentration at equilibrium in solution (mg dm^{-3}),

Q_m = MB concentration when monolayer forms onto particle surface (mg g^{-1}).

PVC in powder form also adsorbed methylene blue and the adsorption isotherm was represented by Langmuir model¹⁹.

Table 1 shows the Langmuir constants of silica, PVC powder and 16% silica film.

The adsorption capacity of a composite material is predicted from the adsorptivity of components by using the "additivity rule" in Equation (2)²¹

Figure 2. SEM micrographs of films with (a) 16% silica with ETD, (b) 16% silica with BSED, (c) 12% silica with ETD, and (d) 12% silica with BSED

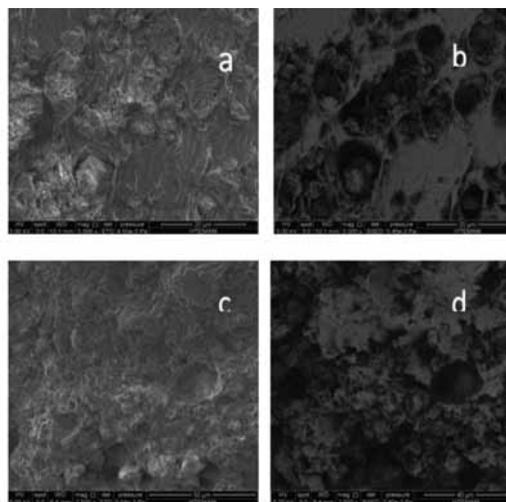


Figure 3. MB Adsorption isotherms of silica (spheres), composite with 13% silica experimental (triangles), theoretical (square)

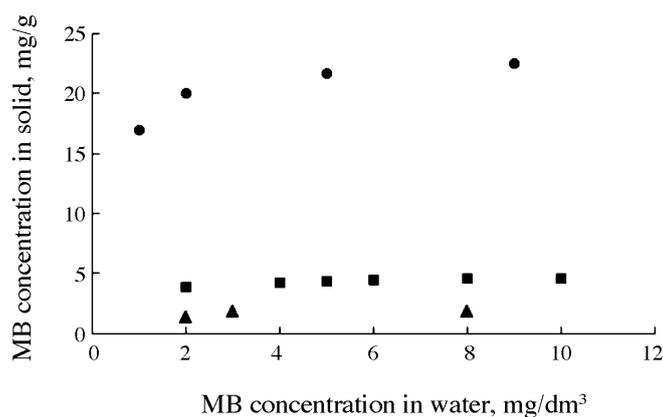


Table 1. Langmuir isotherm constants of the adsorption isotherm of MB on silica powder, PVC powder¹⁹ and 13% SiO_2 composite

Sample	Q_m	K
Silica	23.54	2.7
PVC powder	6.18	1.36
16% SiO_2 composite	2.22	0.97

$$Q_c = \sum Q_i \times m_i \quad (2)$$

Where, Q_c and Q_i are the amount of mass adsorbed on unit mass of the composite and its components, respectively, and m_i is the mass fraction of each component in composite structure.

When PVC was dissolved in DOP, the surface area is reduced and its MB adsorption capacity gets lowered. Also encapsulating silica in the polymer matrix reduced the adsorption capacity. In **Figure 3** the experimental adsorption isotherms of composite with

Figure 4. Change of MB concentration in composites with their silica content for initial MB concentration of 18 mg dm⁻³ in water

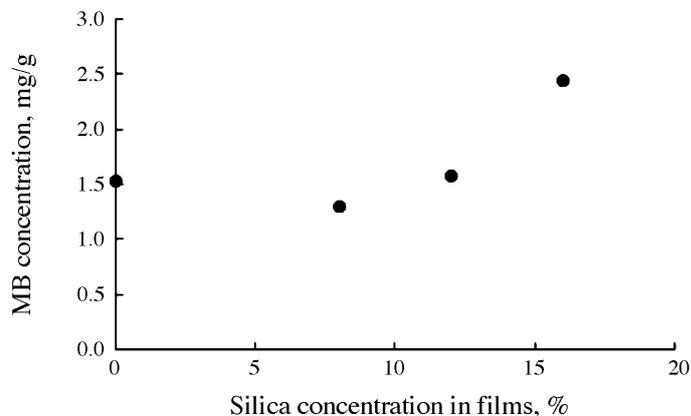


Figure 5. Change of MB concentration with time for initial MB concentration of 18 mg/dm³ for composites having different concentrations of silica

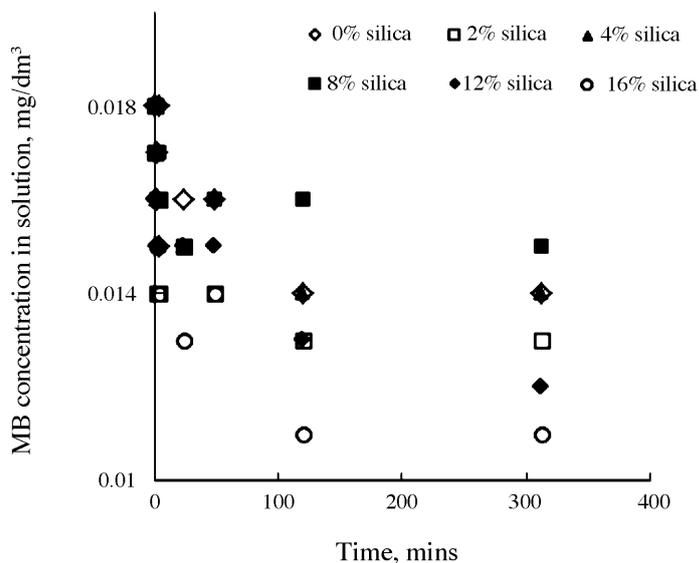
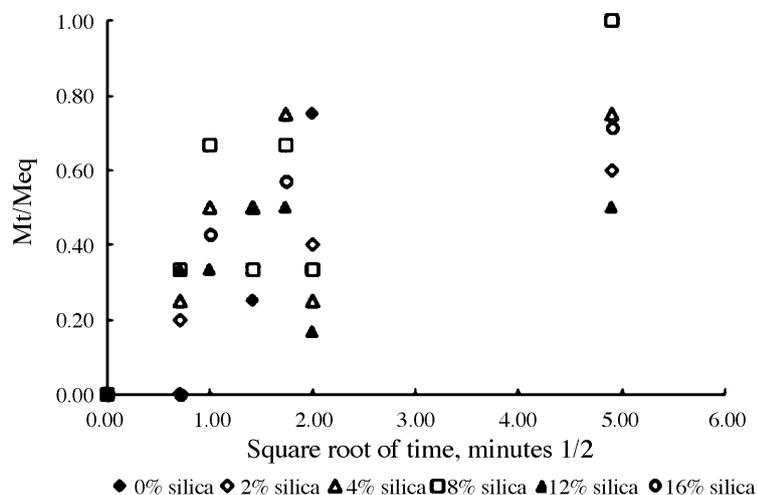


Figure 6. Change of fractional uptake with square root of time



12% silica and predicted values from Equation (3) are shown. However the composites having silica had higher MB adsorption capacity as seen in **Figure 4**.

3.4 MB Adsorption Kinetics

As the MB adsorption process progresses, MB concentration in the solution phase diminishes as seen in **Figure 5**.

The coefficient of diffusion of MB in composites can be obtained carrying out the procedure of classical methods as if the process were Fickian. Equation (3) was used for the evaluation of short time data of adsorption to find out the effective diffusion coefficient.

$$M_t/M_{eq} = (4/l)(D_e t/\pi)^{0.5} \quad (3)$$

Where, M_t and M_{eq} are the adsorbed amount at time t and at equilibrium respectively, l is the diffusion path length, and, D_e is the effective diffusion coefficient.

As seen in **Table 2** the diffusivity of MB in composites is at the order of 10⁻¹¹ m²/s. They exhibit almost the same order of the diffusion coefficient of MB in PVC natural zeolite composites²². The regression coefficients of the linear relations represented by Equation (3) was low (**Table 2**) due to oscillating nature of the adsorption process. The composite without any silica had a higher MB diffusion coefficient since the MB moved in composite without being absorbed.

The objective of the present study is to incorporate the adsorption capacity of silica into a plastic matrix so that to obtain a system which has a high capacity for dye adsorption and is convenient to use in ease for column applications¹⁸ as stacked or pelletized. Using such PVC-silica composite sheets as column packing, the packing time will be reduced and the surface available for diffusion will be increased¹⁸. Therefore, a composite

Table 2. Methylene blue adsorbed at equilibrium for initial MB concentration of 0.018 g/dm³ and solid liquid ratio of 0.03 g/cm³, Diffusion coefficient of the films and their regression coefficient

Silica Conc. %	q _e , mg/g	D of MB x10 ¹¹ , m ² /g	R ² for D
0	1.54	14.6	0.74
2	2.29	1.5	0.84
4	1.99	2.5	0.16
8	1.29	4.5	0.40
12	1.57	4.2	-0.34
16	2.43	3.3	0.60

material having silica incorporated into a plastic matrix composed of plasticized PVC with DOP has been produced and characterized in terms of the adsorption capacity of the system which is a prospective material for dye adsorption.

4. CONCLUSIONS

Plastisol-plastigel technique provides a simple and inexpensive method to produce the flexible PVC-silica composite sheets as column packing for the removal of colored contaminants of industrial waste waters. Although the MB adsorption capacity was extensively high for silica, it was moderate for the composite most likely due to the occlusion of pores of silica by plasticizer to some extent. While the silica component provides high adsorption capacity, PVC matrix keeps the silica particles coherent and hinders the contamination of the solution with dispersed silica. 90% clarification of a 0.02 gdm⁻³ MB solution was achieved through the use of 16% silica containing composite for the solid liquid ratio of 0.12 g/cm³. Since silica component is the main adsorbing site, the more the silica is added into the composite, the higher is the adsorption capacity to be introduced. The apparent diffusivity of the present composites was at the order of 10⁻¹¹ m²/s. Making use of

such PVC-silica composite sheets as column packing, the packing time will be reduced and the surface available for diffusion will be increased.

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