

THE INVESTIGATIONS ON PROCESS TYPE INFLUENCE ON METHYL VIOLET ADSORPTION ON CHITIN AND CHITIN DEACETYLATION PRODUCTS

**Artur Tórz*, Dorota Łącka, Roman Turczyn,
Małgorzata Gnus**

*Department of Analytical Chemistry,
Silesian University of Technology,
ks. M.Strzody 9, 44-100 Gliwice, Poland
e-mail: artur.torzs@gmail.com*

Abstract

The aim of this work was to study various adsorption processes of methyl violet (model compound of aniline dye) on chitin and chitin deacetylation products. Two types of adsorption processes - batch and continuous - were tested. Results illustrated that raw chitin is an effective adsorbent for methyl violet and the adsorption activity of chitin deacetylation products strongly decrease with increasing degree of deacetylation (DDA). The continuous process is more effective than batch process.

Keywords: *chitin, chitosan, adsorption, continuous process, batch process*

Received: 11.05.2015

Accepted: 10.06.2015

1. Introduction

The removal of colour from dye-contaminated wastewater has long been a major environmental problem of the world. Annual market for dyes is more than 7×10^5 tonnes per year and 2% of dyes that are produced are discharged directly in aqueous effluent, and 10% are subsequently lost during the textile coloration process [1]. Synthetic dyes in an small effluent, even in a small amount, are highly visible and have undesired effects not only on the environment, but also on living creatures. Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentrations. There are several methods for dye removal such as biological treatment, coagulation, flocculation, chemical oxidation, membrane processes and adsorption. Most dyestuffs are stable for light and oxidizer and a combination of several processes is generally necessary to achieve adequate removal of all contaminants. At the moment adsorption is a quite effective method for the removal of dyes from wastewater. The most commonly used adsorbent for colour removal is activated carbon [2] but it is relatively expensive.

The increasing demand from consumers and industry for environmentally friendly and renewable polymers explain the great interest for macromolecules as substitutes of synthetic, petroleum-based, polymers. Therefore, many researchers in recent years have focused on the use of various low-cost natural adsorbents like chitin and chitosan [3]. Chitin and its *N*-deacetylated derivative chitosan represent a family of biopolymers, made up of $\beta(1\rightarrow4)$ -linked *N*-acetyl-D-glucosamine and D-glucosamine subunits (amino polysaccharides), and indicate some potential advantages: (1) presence of different functional groups, (2) easy modification and even possibility to use it without preliminary modification, (3) rather high thermal stability and durability. Thus, chitosan could be considered as a “green polymer” of a variety of current and potential application [4].

The purpose of the letter is to present the first attempts of adsorption activity testing of raw materials before chemical/physical modifications in two types of adsorption process. The continuation of this work will be further chemical and/or physical functionalization to obtain biodegradable as well as environmental friendly unique multifunctional monolithic materials with useful properties. Some materials were described in our previous publication [5].

In this study the efficiency of chitin adsorbents in adsorbing model compound of aniline dye (methyl violet) is measured against that of chitin deacetylation products adsorbent. The main objective of this work is to study the influence of type of adsorption process and main process parameters on the equilibrium and kinetics of the adsorption of methyl violet onto four chitin samples.

2. Material and methods

2.1 Materials

Chitin from crab shells (Ch1) was from Sigma (Batch no 067K0026). Chitosan MMW (Ch4) was from Aldrich (Batch no 08028CD). Chitosans samples (Ch2, Ch3) were prepared by deacetylating chitin using 50% NaOH solution at 100 °C for a few hours [6]. The DDA of all samples determined by conductometric titration (own method). Descriptions of all prepared samples are summarized in Table 1.

Table 1. Characteristic of the samples.

Sample	DDA [%]
Ch1	12.5
Ch2	56.1
Ch3	73.4
Ch4	88.6

Methyl violet 3B was from GURR (England). The chemical formula and molecular structure of this dye is shown in Table 2. The dye was used as supplied without further purification.

Table 2. The physical characteristics and molecular structure of methyl violet dye.

Dye name	Methyl violet 3B
λ_{max} [nm]	586
Chemical formula	$C_{24}H_{28}ClN_3$
Molecular structure	

2.2 Methods

2.2.1 Batch process

A typical adsorption experiments were carried out by adding a fixed amount of sorbent (400 mg) into a beaker with definite volume (250 mL) of dye solution (initial concentration 6 mg/L) without changing pH (pH 6.3±0.3). The beaker with dye solution were placed in a thermostatic water-bath shaker and agitation was provided at 200 rpm for 180 minutes to ensure equilibrium was reached.

2.2.2. Continuous process

In case of flow adsorption experiments a fixed amount of sorbent (400 mg) were carried out into a glass column of about 1.0 cm internal diameter and 10 cm length. The beaker with dye solution (initial concentration 6 mg/L) without changing pH (pH 6.3±0.3) were placed in a thermostatic water-bath shaker and agitation was provided at 200 rpm. The dye solution was allowed to flow through the column in closed circuit system at a constant flow rate (25 mL/min) throughout the experiment by a peristaltic pump. The process were carried out for 180 minutes to ensure equilibrium was reached.

2.2.3. Analysis

In both processes the dye concentration were measured any 15 minutes by UV/VIS spectrophotometer (UV-VIS HP-8452 A) at 586 nm wavelength and the dye removal efficiency X [%] were calculated as follows:

$$X = \frac{C_0 - C_t}{C_0} \cdot 100$$

where: C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and any time, respectively.

3. Results and discussion

3.1. Effect of contact time

The contact time between adsorbate and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of adsorbates and establishment of equilibrium in a short period signify the efficacy of that adsorbent for its use in wastewater treatment. To determine the equilibration concentration and time, the adsorption of methyl violet onto chitin and chitin deacetylation products were studied as a function of contact time for initial dye concentration of 6 mg/L at 303, 323 and 343 K and solution pH=6.3±0.3. Sorbent dosage was 400 mg for 250 mL of dye solution. Dye solutions were kept in contact with sorbent for 180 minutes although no significant variation in residual dye concentration was detected any 15 minutes. Figures 1 and 2 presents the effect of contact time in batch and flow process respectively. The contact time curve shows that the dye removal was rapid in the first 15 min. The curves of contact time are single, smooth and continuous leading to saturation. In all cases the equilibrium condition was achieved within 180 minutes in both types of processes.

3.2 Effect of temperature

The investigations on process type influence on methyl violet adsorption on chitin and chitin deacetylation products

Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. The effect of temperature on the adsorption of methyl violet on chitin from crab shells was investigated at 303, 323 and 343 K. The results of the influence of temperature on dye removal efficiency in bath process was presents on Figure 1, and in flow process in Fig. 2. It has been observed that an effectiveness of both process strongly depends of thermal conditions of experiments and decreases with increasing of temperature. These results are in good agreement with sorption theories widely described in a literature.

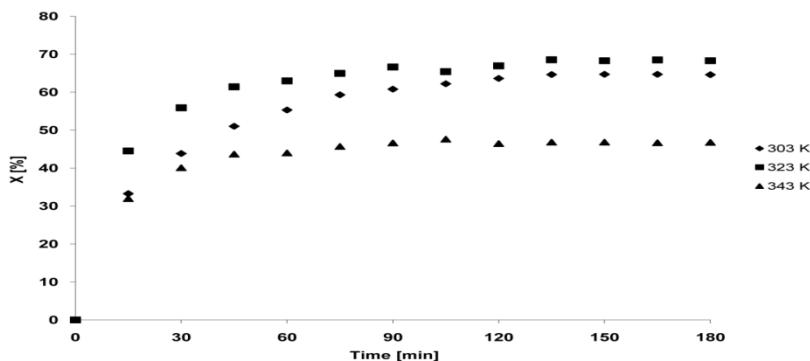


Figure 1. The influence of contact time and temperature on dye removal efficiency for chitin from crab shells (DDA=12,5%) in batch process.

3.3 Effect of degree of deacetylation (DDA)

Figures 3 and 4 presents results of sorption experiments according to both kinds of processes which were obtained for samples of different DDA. In case of periodic load changes it has been observed an inversely relations between deacetylation degree of the bulk polymer bed and dye removal efficiency. However an interesting phenomena has been observed if take under account the flow process; the dependence of discussed parameters exhibit distinct minimum at field of DDA~50% as clearly has been shown in Fig. 5. It is probably due to a chemisorption proceeded in such conditions nevertheless it should be explained by realizing further experiments.

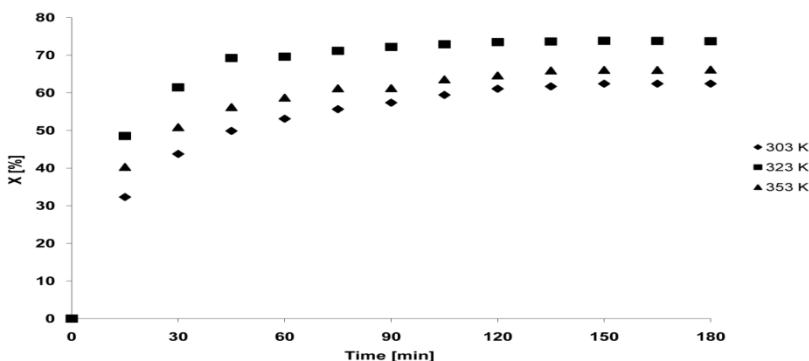


Figure 2. The influence of contact time and temperature on dye removal efficiency for chitin from crab shells (DDA=12,5%) in flow process.

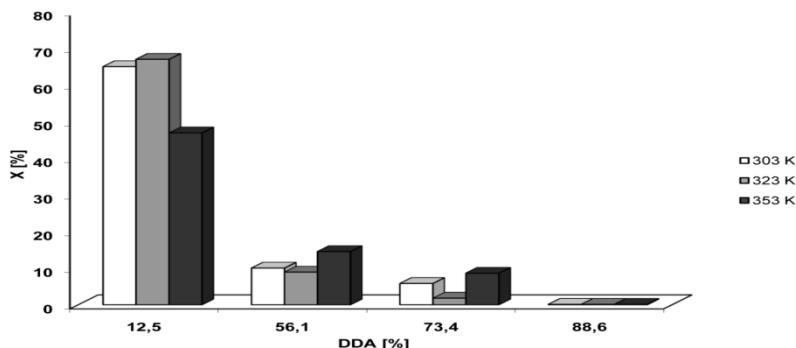


Figure 3. The influence of degree of deacetylation and temperature on dye removal efficiency for chitin and chitosan samples in batch process.

3.4 Effect of process type

As shown in Fig. 1 and 2., the maximum effectiveness of removal of methyl violet by adsorption on chitin from crab shells of DDA=12,5% in bath process (68.5 %,) was observed at 323 K. The higher values of the parameter obtained in case of flow conditions at the same parameters of experiments (ex. 73.8%, T= 323 K) prove better efficiency of dynamic processes if compare with static ones in relation to waste water treatment. It may be caused by probable increasing of a significance of absorption effects characteristic for a flow mass transfer phenomena.

The investigations on process type influence on methyl violet adsorption on chitin and chitin deacetylation products

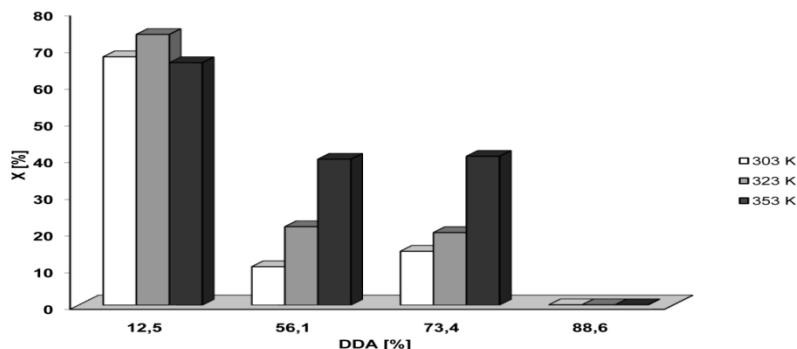


Figure 4. The influence of degree of deacetylation and temperature on dye removal efficiency for chitin and chitosan samples in flow process.

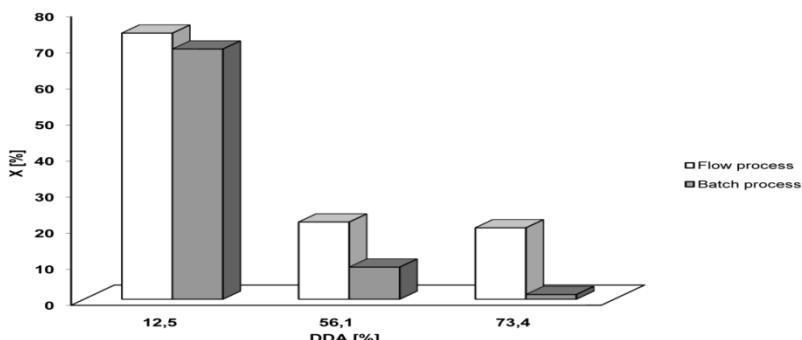


Figure 5. The influence of process type and degree of deacetylation on dye removal efficiency.

4. Conclusions

Two types of adsorption processes (batch and continuous) were tested. The present study shows that the chitin and chitin deacetylation products are an effective adsorbent for removal of methyl violet from aqueous solution. The rate of adsorption of methyl violet onto tested materials were initially very high, then was followed by a slower rate and gradually approached a plateau. Raw chitin is an effective adsorbent for methyl violet and the adsorption activity of chitin deacetylation products decrease with increase of degree of deacetylation (DDA). In all cases the continuous process is more effective than bath process.

5. Acknowledgements

*Our cordially thanks for Prof. James H. Clark for the inspiration.
Progress on Chemistry and Application of Chitin and its Derivatives, Volume XX, 2015*

6. Reference list

1. Pearce CI, Lloyd JR., Guthrie JT; (2003) The removal of colour from textile wastewater using whole bacterial cells: a review, *Dyes and Pigments*, 58, 179–196. **DOI:** 10.1016/S0143-7208(03)00064-0
2. McKay G; (1982) Adsorption of dyestuffs from aqueous solutions with activated carbon. I. Equilibrium and batch contact-time studies, *J. Chem. Technol. Biotechnol.* 32, 759–772. **DOI:** 10.1002/jctb.5030320712
3. Bhatnagar A, Sillanpää M; (2009) Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater — A short review, *Adv. Colloid Interf. Sci.* 152, 26-38. **DOI:** 10.1016/j.cis.2009.09.003
4. Ravi Kumar MNV; (2000) A review of chitin and chitosan applications, *Reactive Funct. Polym.* 46, 1-27. **DOI:** 10.1016/S1381-5148(00)00038-9
5. Krzesinska M, Torz A, Zachariasz J, Muszynski J, Socha J, Marcinkowski A; (2007) New chitosan/CEG (compressed expanded graphite) composites—preparation and physical properties, *Green Chemistry*, 9, 842-844. **DOI:** 10.1039/B700740J
6. Horton D, Lineback DR; (1965) N-Deacetylation: chitosan from chitin. In: Whistler R. L. (ed.), *Methods in Carbohydrate Chemistry*, Vol. 5, General Polysaccharides, Academic Press, New York, 403-406.