

# EFFECTIVENESS OF DYE ADSORPTION ONTO NON-CROSS-LINKED AND CROSS-LINKED CHITOSAN BEADS

**Urszula Filipkowska**

*Department of Environmental Protection Engineering,  
University of Warmia and Mazury in Olsztyn  
ul. Prawocheńskiego 1, 10 – 957 Olsztyn, Poland  
E-mail: urszula.filipkowska@uwm.edu.pl*

## **Abstract**

*The study was established to analyze the effectiveness of Reactive Black (RB5) and Basic Green (BG4) dyes adsorption onto chitosan beads and onto chitosan beads cross-linked with glutaraldehyde depending on the initial dye concentration in the solution (1, 5, 100 and 200 mg/dm<sup>3</sup>). It demonstrated that both the initial concentration of dye in the solution as well as the type of adsorbent affected the effectiveness of the adsorption process. An increase in the initial dye concentration in the solution was increasing adsorption effectiveness, irrespective of the type of dye and adsorbent. The cross-linking of chitosan beads with glutaraldehyde turned out to be beneficial only in the case of the RB5 dye.*

**Key words:** *adsorption, dyes, chitosan beads, cross-linked chitosan beads, glutaraldehyde.*

## 1. Introduction

Chitosan is a product of deacetylation process of chitin which, next to cellulose, is the most popular natural polymer that has increasingly been applied in medicine, pharmacology, biotechnology, as well as plant or environment protection. It is produced through the deacetylation of chitin which is the most abundant natural biopolymer. Because chitin is a waste product of the sea foods processing industry (shells of shrimps, crabs and lobsters) [1, 2], it is acknowledged as an easily-available and inexpensive sorbent.

Owing to the fact that it possesses amine and hydroxyl functional groups, it is characterized by a high adsorption effectiveness of metal ions [3 - 5] and dyes from aqueous solutions [6,7,8]. Depending on the type of dye and conditions of the sorption process, the maximum sorption capacity of chitosan may exceed 1000 mg/g [9]. A drawback of chitosan is its solubility in acidic solutions. At  $\text{pH} < 5.5$ , it is being dissolved and loses its capacity for sorbates binding. A solution to this problem may be its cross-linking. The cross-linked chitosan maintains constant reactivity in a wide pH range and is characterized by high mechanical resistance [10 - 12]. The cross-linking may also affect the improvement of its regeneration properties [13]. The cross-linking agents may, however, evoke changes in the sorption capacity of chitosan. Depending on the type of cross-linking agent applied, conditions of the sorption process and type of the dye being adsorbed, the maximum sorption capacity of the resultant sorbent may increase to  $1700 \text{ mg/dm}^3$  [14],  $1800 \text{ mg/dm}^3$  [15] and even to  $2498 \text{ mg/dm}^3$  [6], or may decrease due to the blocking of part of the functional groups (amine or hydroxyl ones) [10].

The objective of this study was to determine the effectiveness of dyes removal from an aqueous solution with the adsorption method, using non-cross-linked chitosan and chitosan cross-linked with glutaraldehyde, depending on the initial concentration of dye in the solution. Analyses were conducted for two dyes: anionic dye – Reactive Black 5 (RB5), and cationic dye – Basic Green 4 (BG4). Chitosan in the form of beads and chitosan cross-linked with glutaraldehyde also in the form of beads was used as an adsorbent.

## 2. Materials and methods

### 2.1 Dyes

Due to their common application, the following two dyes: RB5 (anionic dye) and BG4 (cationic dye) were used in the study (*Table 1*).

### 2.2 Sorbent

#### *Preparation of chitosan beads*

Analyses were conducted with chitin of krill obtained from the Sea Fisheries Institute in Gdynia, with dry matter content of 95.64%, ash content of 0.32%, and deacetylation degree below 3%. Before sorption, commercial chitin was rinsed with distilled water and 6 N hydrochloric acid in order to loosen its structure and wash out calcium ions, magnesium ions and lipid residues, next rinsed with distilled water until a neutral reaction of the filtrate. Afterwards, chitin was cooked for 3h on a water bath with 70% potassium base. After

**Table 1.** Characteristics of the dyes examined.

Dye	Structural formula	Molecular weight, g/mole
Reactive Black 5		991
Basic Green 4		927

cooling, the chitin was again flushed with distilled water until a neutral reaction and filtrated off under vacuum. Deacetylation degree amounted 75%.

50 g of chitosan dissolved in 5% acetic acid were instilled with a micropipette to 5% NaOH and left in the solution for 24 h. The size of the instilled beads was controlled by the size of the micropipette and was 3 mm. The resultant beads were filtrated, rinsed with distilled water and kept in distilled water until used.

#### **Preparation of cross-linked chitosan beads**

Chitosan beads were fixed in a solution of a cross-linking agent – glutaraldehyde. The cross-linking agent to chitosan ratio reached 1 : 1 (w/w). The cross-linked chitosan beads were rinsed with distilled water in order to remove the unreacted glutaraldehyde.

### **2.3 Analytical procedures**

Analyses were carried out to determine adsorption effectiveness of two dyes: anionic RB5 and cationic BG4, at four initial concentrations: 1, 5, 100 and 200 mg/dm<sup>3</sup>, and onto two adsorbents: chitosan beads and chitosan beads cross-linked with glutaraldehyde. The adsorption of RB5 dye was assayed at pH = 3.0, whereas that of BG4 dye at pH = 9.0.

To this end, 0.1 g sorbent/dm<sup>3</sup> portions (1 g d.m. sorbent/dm<sup>3</sup>) were weighted into 10 Erlenmeyer's flasks 200 dm<sup>3</sup> in volume, and the flasks were then filled with 100 cm<sup>3</sup> of a dye solution with concentrations of 1, 5, 100 and 200 mg/dm<sup>3</sup>. Thus prepared samples were placed in a shaker for 2 h, at the speed of '200' and vibration amplitude of '9'. Afterwards, the samples were sedimented for 1 min, and extinction was measured with a UV-VIS

**Table 2.** Wavelength at extinction measurement of the dyes examined

Dyes	Wavelength $\lambda$ , nm
RB5	597
BG4	355

SP 3000 spectrophotometer. All analyses were carried out in 10 replications. Analogous procedures were applied for each adsorbent, dye and initial dye solution in the solvent.

## 2.4 Analytical methods

In each of the samples, the concentration of dye left in the aqueous solution was determined spectrophotometrically. Samples to be analyzed were collected (10 cm<sup>3</sup>), decanted and centrifuged for 15 min at 10,000 rpm. The concentration of the remaining dye was determined acc. to standard curves in a UV-VIS Spectrophotometer SP-3000.

Wavelength at which extinction was read out was determined for each of the analyzed dyes (**Table 2**).

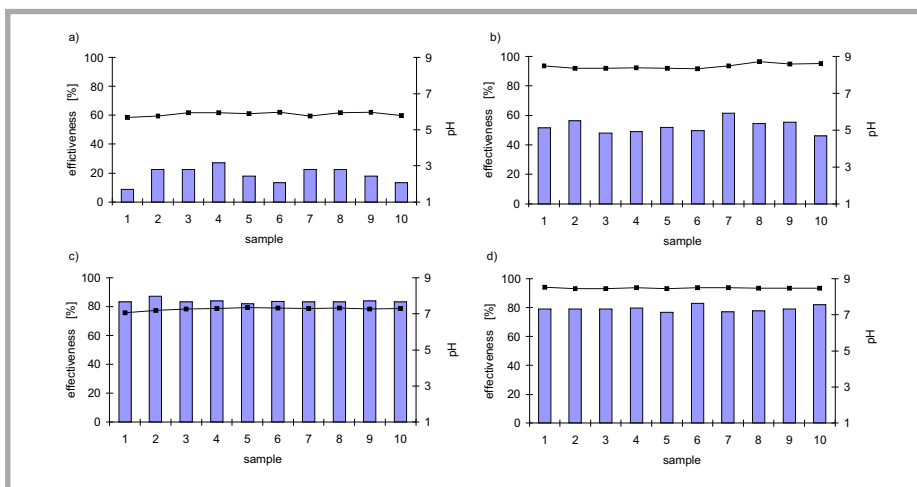
## 3. Results and discussion

The effectiveness of the adsorption process of two dyes: anionic RB5 and cationic BG4, depending on their initial concentration and type of adsorbent was analyzed based on the concentration of dye left in the solution  $C_K$  (mg/dm<sup>3</sup>). The conducted study enabled determining the effect of the type and initial concentration of dye in the solution on the effectiveness of the adsorption process.

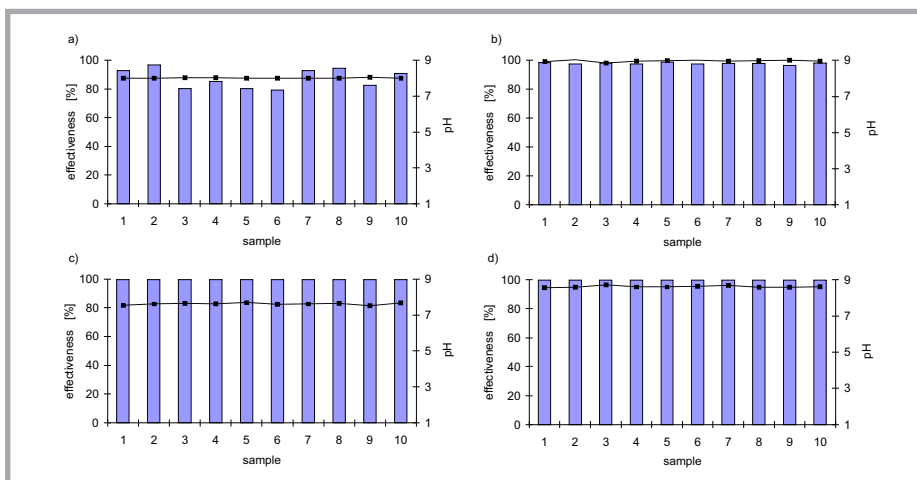
**Figures 1 & 2** depict results of the effectiveness of the adsorption process onto chitosan beads depending on the initial concentration of RB5 and BG4 dyes as well as end pH values on completion of the adsorption process.

Based on the conducted analyses it may be observed that the adsorption onto chitosan beads depended on the type of dye tested and, irrespectively of the initial dye concentration in the solution, was higher for the BG4 dye. In the case of the RB5 dye, the effectiveness of dye removal was observed to be significantly affected by the initial dye concentration in the solution. At low initial concentrations, i.e. 1 and 5 mg/dm<sup>3</sup>, the mean effectiveness of RB5 adsorption reached 18.72 and 52.4%, respectively, and was lower than the respective values recorded at higher initial concentrations of the dye, i.e. 100 and 200 mg/dm<sup>3</sup>. In the case of the two higher concentrations examined, the increase in dye content of the solution did not influence the effectiveness of the adsorption process – it was comparable for both concentrations and reached 79.3%.

The adsorption process of the RB5 dye in all experimental series, irrespectively of the adopted initial concentration of dye in the solution, was begun at pH 3.0, whereas that of BG4 at pH 9.0. In the case of the anionic dye, a tangible dependency was observed between the effectiveness of RB5 removal and solution's pH after the adsorption process. At the lowest assumed initial concentration, i.e. 1 mg/dm<sup>3</sup>, the least increase was noted in pH



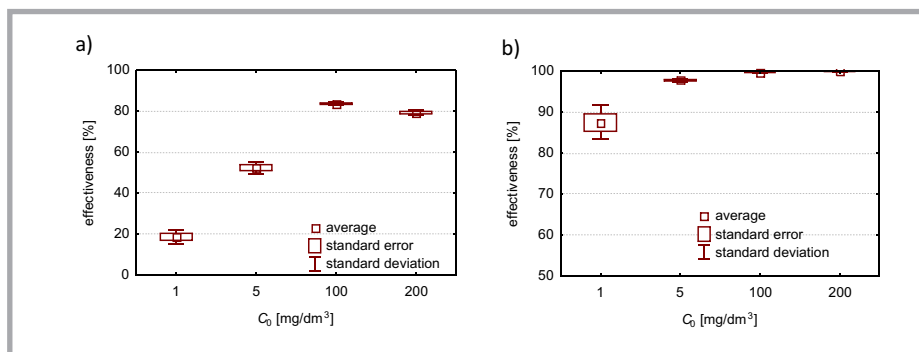
**Figure 1.** Effectiveness of the adsorption process of RB5 dye and pH values after adsorption onto chitosan beads at different initial concentrations of dye in the solution. a) 1 mg/dm<sup>3</sup>, b) 5 mg/dm<sup>3</sup>, c) 100 mg/dm<sup>3</sup>, d) 200 mg/dm<sup>3</sup>.



**Figure 2.** Effectiveness of the adsorption process of BG4 dye and pH values after adsorption onto chitosan beads at different initial concentrations of dye in the solution. a) 1 mg/dm<sup>3</sup>, b) 5 mg/dm<sup>3</sup>, c) 100 mg/dm<sup>3</sup>, d) 200 mg/dm<sup>3</sup>.

value after reaching the equilibrium concentration, namely from 3.0 pH to 5.7 pH. In the other series, the effectiveness of the anionic dye (RB5) removal was linked with pH value increase in the solution after adsorption from 7.3 to 8.4 pH.

Analogous results were achieved by Chiou et al. (2003), who were investigating the effect of the initial concentration of Metanil Yellow (MY) and Reactive Blue 15 (RB 15) dyes



**Figure 3.** Average effectiveness of adsorption onto chitosan beads at different initial concentrations of dye in the solution. a. RB5, b. BG4.

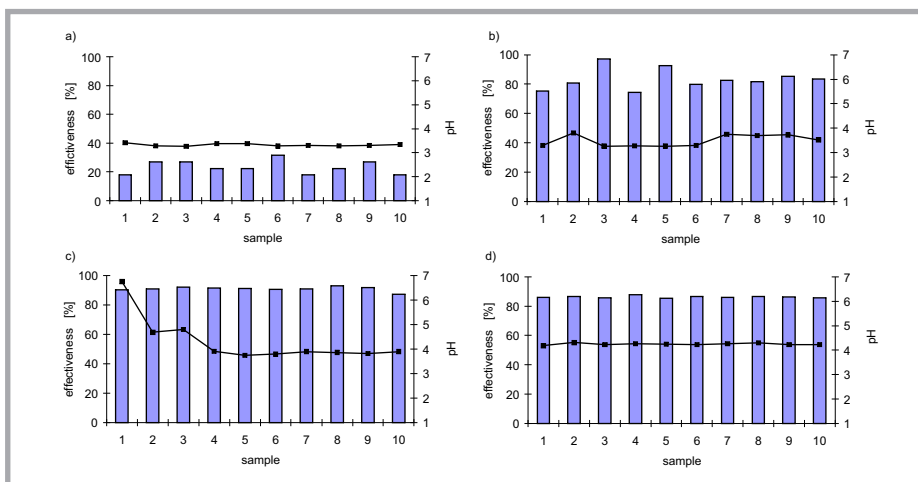
on adsorption effectiveness onto cross-linked chitosan beads used as an adsorbent. The cross-linking agent was epichlorohydrin (ECH). Results obtained by those authors demonstrated the initial dye concentration to affect the improvement in adsorption effectiveness. An increase in the initial concentration of dye resulted in enhanced effectiveness of the process. At the initial concentration of RB 15 dye reaching: 0.55, 0.81, 0.97 and 1.36 mmol/dm<sup>3</sup> the effectiveness of dyes removal by chitosan accounted for: 45, 71, 89 and 99%, whereas at initial concentrations of MY dye reaching 3.78 and 5.63 mmol/dm<sup>3</sup> it accounted for 36 and 100%, respectively.

In the reported study, such a tendency was not observed in the case of the second dye examined, i.e. BG4. The non-cross-linked chitosan beads turned out to be a good adsorbent, irrespective of the initial dye concentration. An insignificantly lower effectiveness – 87.5% – was achieved for the initial concentration of 1 mg/dm<sup>3</sup>. In the case of the other analyzed concentrations, adsorption effectiveness was high and ranged from 97.8 to 99.9%.

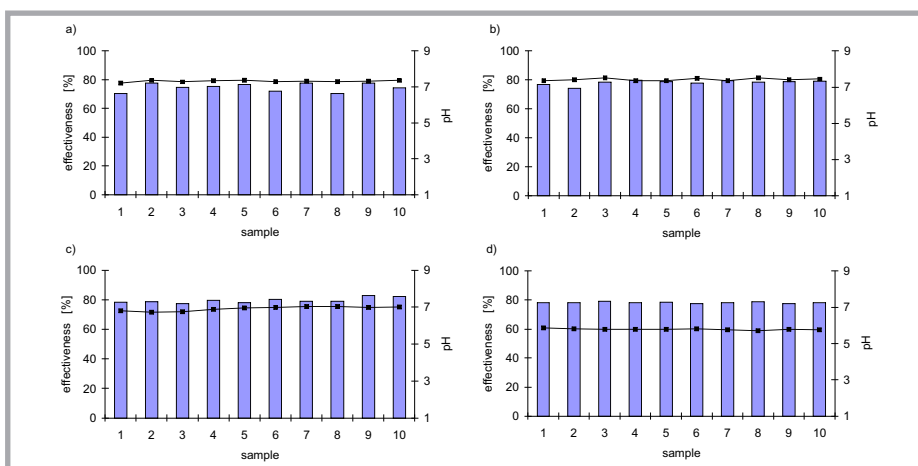
The statistical analysis of the results indicates that values of standard deviation were diminishing along with the increasing dye concentration in the solution (**Figure 3**).

**Figures 4 & 5** present results of adsorption effectiveness as well as end pH values on completion of the adsorption process as affected by the initial concentration of RB5 and BG4 dyes in the solution, for chitosan beads cross-linked with glutaraldehyde used as an adsorbent.

The study demonstrated that changing properties of the adsorbent, namely chitosan beads, through cross-linking with glutaraldehyde had a positive effect on the effectiveness of RB5 dye adsorption. The increased effectiveness was reported at all initial dye concentrations examined. At three initial concentrations tested in the study: 5, 100 and 200 mg/dm<sup>3</sup>, the effectiveness of dye adsorption reached ca. 90%. In the case of the lowest initial dye concentration, i.e. 1 mg/dm<sup>3</sup>, it was lower and reached 23% (**Figure 4**).



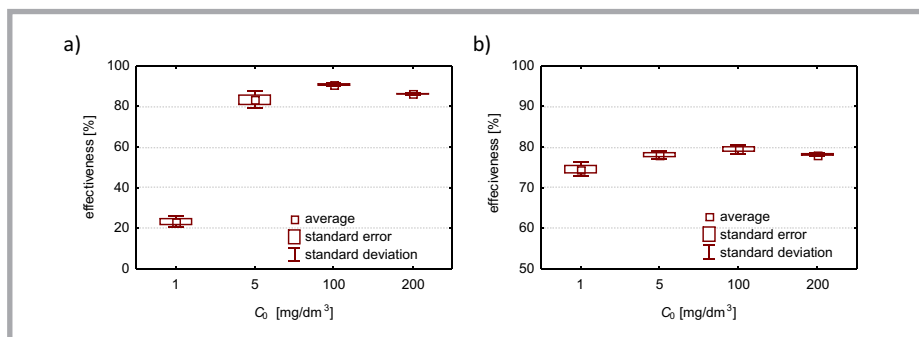
**Figure 4.** Effectiveness of the adsorption process of RB5 dye and pH values after adsorption onto chitosan beads cross-linked with glutaraldehyde at different initial concentrations of dye in the solution. a) 1 mg/dm<sup>3</sup>, b) 5 mg/dm<sup>3</sup>, c) 100 mg/dm<sup>3</sup>, d) 200 mg/dm<sup>3</sup>



**Figure 5.** Effectiveness of the adsorption process of BG4 dye and pH values after adsorption onto chitosan beads cross-linked with glutaraldehyde at different initial concentrations of dye in the solution. a) 1 mg/dm<sup>3</sup>, b) 5 mg/dm<sup>3</sup>, c) 100 mg/dm<sup>3</sup>, d) 200 mg/dm<sup>3</sup>

The increase in pH value after completion of the adsorption process was not as significant as in the case of RB5 adsorption onto non-crosslinked chitosan beads, which may indicate different binding of the RB5 dye onto chitosan beads cross-linked with glutaraldehyde.

The cross-linking of chitosan beads with glutaraldehyde caused a decrease in the effectiveness of BG4 adsorption, irrespective of its initial concentration in the solution. The



**Figure 6.** Average effectiveness of adsorption onto chitosan beads cross-linked with glutaraldehyde at different initial concentrations of dye in the solution. a) RB5, b) BG4.

mean values of effectiveness did not exceed 80% and were ranging from 74.6 to 79.5% (Figure 5). This was confirmed by the statistical analysis of results achieved (Figure 6).

An opposite tendency, compared to BG4 adsorption onto non cross-linked chitosan, was also observed in the case of pH values in the solution after completion of the adsorption process. The adsorption of BG4 onto non cross-linked chitosan beads did not cause any significant changes in pH value, whereas in all series with chitosan beads cross-linked with glutaraldehyde used as an adsorbent a decrease was simultaneously noted in pH value to 5.8 – 7.3 pH, compared to the initial value of 9.0 pH.

An overview of literature data indicates that the type of the cross-linking agent determines properties of the modified adsorbent. Reactions of cross-linking may be of homogenous or heterogenous character, and consist in the chemical modification of chitosan by incorporating new functional groups into structures of its polymeric chains, with the use of two or more functional cross-linking compounds. The extent of chitosan cross-linking depends on a variety of factors, including: deacetylation of chitin, concentration of cross-linking, temperature and time of the reaction [3, 17, 18]. The cross-linking agents may include, e.g.: glutaraldehyde, epichlorohydrin or glycoethylene. Upon the action of the cross-linking agent, special networks are being formed, which diminish the mobility of polymer chains through the generation of new links between those chains.

The change in chitosan properties as a result of cross-linking enabled the adsorption of anionic dye RB5 at pH = 3.0, by eliminating chitosan dissolution at a low pH value. The cross-linking of chitosan with glutaraldehyde evoked a change in functional groups which enhanced the adsorption of RB5 dye, but was unfavorable in the case of the BG4 dye.

## 4. Conclusions

The initial concentration of dye in the solution turned out to significantly affect adsorption effectiveness of the analyzed dyes. The effectiveness was observed to increase along with the increasing initial dye concentration. The greatest impact of dye concentration



was noted in the case of RB5 adsorption onto non-cross-linked chitosan beads. Adsorption effectiveness at the lowest analyzed initial dye concentration was lower by almost 60% than the respective value recorded at the highest concentration – 200 mg/dm<sup>3</sup>.

The cross-linking of chitosan beads was found to exert a positive effect on removal effectiveness of anionic dye RB5. The effectiveness was increasing, irrespective of the initial concentration of the dye. The effectiveness of adsorption onto cross-linked chitosan beads at the initial dye concentration of 5 mg/dm<sup>3</sup> was higher by over 30% than that reported for the non-cross-linked chitosan. An opposite tendency was noted for the BG4 dye, in the case of which – irrespective of its initial concentration – the effectiveness of adsorption was lower by over 20% onto cross-linked chitosan beads compared to the non-cross-linked beads.

#### **4. References**

1. Kumar MNVR; (2000). A review of chitin and chitosan applications. *React Funct Polym* 46, 1–27.
2. Longhinotti E, Pozza F, Furlan L, Sanches MNM, Klug M, Laranjeira MCM, Fávère VT; (1998). Adsorption of anionic dyes on the biopolymer chitin. *J Braz Chem Soc* 9, 435–440.
3. Chiou MS, Li H.Y; (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *J Hazard Mat* 93(2), 233–48.
4. Guibal E, Milot C, Tobin JM; (1998) Metal-anion sorption by chitosan beads: equilibrium and kinetic studies. *Ind Eng Chem Res* 37,1454–1463.
5. Liu XD, Tokura S, Haruki M, Nishi N, Sakairi N; (2002) Surface modification of nonporous glass beads with chitosan and their adsorption property for transition metal ions. *Carbohydr. Polym.* 49: 103–108.
6. Chiou MS, Ho PY, Li HY; (2004) Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes Pigments* 60, 69–84.
7. Juang RS, Tseng RL, Wu FC, Lee SH; (1997) Adsorption behavior of reactive dyes from aqueous solutions on chitosan. *J Chem Technol Biotechnol* 70, 391–399.
8. Wu FC, Tseng RL, Juang RS; (2001) Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. *J Hazard Mater B81*, 167–177.
9. Chiou MS, Li HY; (2002) Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *J Hazard Mater* 93(2), 233–48.
10. Tomczak E; (2007) Równowaga sorpcyjna na modyfikowanych kulkach chitozanowych. *Proceedings of ECOPol Vol. 1, No ½*.
11. Wan Ngah WS, Ghani SA, Kamari A; (2005) Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresour Technol* 96, 443–450.
12. Wan Ngah WS, Kamari A, Koay YJ; (2004) Equilibrium and kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads. *Int J Biol Macromol.* 34, 155–161.
13. Wan Ngah WS, Kamari A, Chong MY, Cheah ML; (2009) Sorption of acid dyes onto GLA and H<sub>2</sub>SO<sub>4</sub> cross-linked chitosan beads. *Desalination.* 249, 1180–1189.
14. Yoshida H, Okamoto A, Kataoka T; (1993) Adsorption of acid dye on cross-linked chitosan fibers: equilibrium. *Chem. Eng. Sci.* 48, 2267–2272.
15. Chiou MS, Li HY; (2003). Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere.* 50, 1095–1105.

16. Juang RS, Tseng RL, Wu FC, Lee SH; (1997) Adsorption behavior of reactive dyes from aqueous solutions on chitosan. *J. Chem. Technol. Biotechnol.* 70, 391–399.
17. Chiou MS, Kuo WS, Li H,Y; (2003) Removal of Reactive Dye from Wasterwater by Adsorption Using ECH Cross – Linked Chitosan Beads as Medium *J Environ Scien and Health*, 38(11); 2621 – 2622.
18. Hasan M, Ahmad AL, Hameed BH; (2008) Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads *Chem Eng J* 136(2-3); 164-172.