Efficiency of Black DN Adsorption onto Chitin in an *Air-Lift* Reactor

U. Filipkowska

Faculty of Environmental Sciences and Fisheries, University of Warmia and Mazury, ul. Prawocheńskiego 1, 10-957 Olsztyn, Poland

Received: 28 July 2003
Accepted: 26 February 2004

Abstract

The efficiency of reactive dyes adsorption onto chitin under dynamic conditions was determined. The research was carried out in an *air-lift* reactor. A reactive dye with chlorotriazine moiety − Black DN was used. The effect of inlet Black DN concentration, chitin concentration in the reactor and flow rate on the maximum adsorption capacity of chitin under dynamic conditions, on the utilisation of the adsorption capacity of chitin and on the real working time of the reactor were investigated. The results showed that the maximum adsorption capacity of chitin was affected most by inlet dye concentration. The utilisation of the adsorption capacity of chitin, at the assumed effectiveness of dye removal, depended on inlet dye concentration and chitin concentration in the reactor. The highest efficiency was obtained at the chitin concentration in the reactor of 5 g/dm^3, inlet dye concentration of 100 mg/dm^3 and flow rate of 0.1 V/h.

Keywords: adsorption, reactive dye, *air lift* reactor, efficiency

Introduction

The majority of studies concerning adsorption were carried out under laboratory conditions in sequencing reactors. The results proved the impact of the kind of adsorbent and adsorbate on the efficiency of dye removal from the solution. It was claimed that reactor configuration and hydraulic conditions could influence the adsorption efficiency to a high extent. In dynamic systems, the investigations on dye removal have been carried out in beds, and peat [1], wood [2] and activated carbon [3] were tested as column packing.

The investigations of colour removal under dynamic conditions by adsorption have been carried out in different types of reactors. They have mainly focused on the determination of optimal parameters, such as retention time, inlet dye concentration or loading. Different kinds of packing were tested as adsorbents.

Zhang [4] designed and tested three different reactor configurations for decolourization of an azo dye, Orange II, with white rot fungus.

Rodríguez, Couto [5] reported a preliminary design of a new photochemical reactor and its application for photochemical degradation of two dyes, Crystal Violet and Azure B, belonging to different structural groups.

Depending on the method of supplying energy, three basic groups of reactors can be distinguished: mechanical, pneumatic and hydraulic reactors.

Air-lift columns are circulating reactors working in the system liquid-gas-solid and for the sake of their advantages they can be used in biotechnology and wastewater treatment.

Air-lift reactors are characterized by a simple construction and a lack of mobile pieces. In comparison with the reactors with stirrers, *air-lift* reactors use about 3-fold less energy, whereas when compared to barbotage columns, they demonstrate better mixing, the ability of keeping suspended solids and better conditions of mass exchange. The drawbacks of the *air-lift* reactors are: their limited use for media of low viscosity and considerable foaming [6]. In the case of Black DN adsorption onto chitin, both limitations are not significant and do not influence the efficiency of the process.

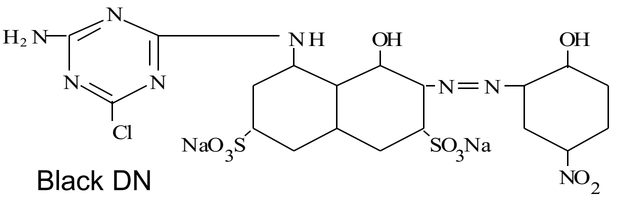

Fig. 1. Chemical structure of Black DN.

Many studies in such reactors have so far concerned hydrodynamic research and determination of the rate of oxygen transport [7, 8]. The correct design and scale-up of an *air-lift* reactor must be based on considering it as the sum of different regions, each with a characteristic flow pattern [9, 10, 11].

Knowledge on the design of dye removal in *air-lift* reactors and their operating conditions is still unsatisfactory. There is no data concerning the effect of technological parameters, such as flow rate, dye concentration in the solution, adsorbent concentration in the reactor on the efficiency of the process. For this reason, research has been undertaken into evaluating the possibilities of the use of *air-lift* reactors in dyes adsorption from water solutions with chitin as an adsorbent.

Even small dye concentration, ca. 1 mg/dm^3, in treated effluent or in water is distinctly visible and causes considerable deterioration of the physico-chemical features. Thus, there is a necessity for working out methods that will enable removal of dyes with almost 100% efficiency.

In this work, the effect of inlet dye concentration, chitin concentration and flow rate on a degree of using the maximum adsorption capacity of chitin under dynamic conditions and on the real working time of the reactor at assumed efficiency of colour removal was investigated.

The aim of the study was to describe the conditions of the *air-lift* reactors which can affect the efficiency of the process and practical usage of the reactor. Dye concentration and flow rate were taken as a design criterion. The amount of dye adsorbed by chitin, at assumed process efficiency, would not be lower than 60% of the maximum adsorption capacity of chitin.

Experimental Procedures

Chitin Preparation and Characteristics

The krill chitin (polymorphic structure α from the Sea Fisheries Institute in Gdynia) was used in the experiment. The chitin was prepared according to the methodology described by Stanley [12]. The adsorbent was waterlogged and left for 24 hours to expand. Then the water was separated and the chitin was washed with a 6 N HCl solution. After washing with distilled water to reach a filtrate of pH 7, the chitin was boiled in a 5 N KOH solution at 100^{0}C for 3 h. The average size of a chitin flake used in the experiment was 314x184 μm. The size of the maximal flake was 756x434 μm, and that of the minimal - 62x62 μm. The chitin flake characteristics is presented in Table 1.

Table 1. Chitin flakes characteristics.

Parameters		Chitin
Deacetylation degree − DD	(%)	5
Dry weight of adsorbent	(%)	95.64
Ash	(%)	0.32
Swollen adsorbent hydratation	(%)	70
Elemental analysis	(%)	C = 43.9 N = 6.4 H = 6.7

Dye Preparation

The chlorotriazine reactive dye Black DN from "Boruta" SA Dye Plant in Zgierz was used in the experiment. The chemical structure of Black DN is shown in Fig. 1.

Analysis of the Efficiency of Black DN Adsorption onto Chitin in an *Air-Lift* Reactor

The scheme of an *air-lift* reactor is shown in Figure 2. Use was made of a reactor of a circular section made of plexiglass, with a diameter of 0.15 m, height of 1.35 m, and active volume of 17 dm^3. In the lower part of the reactor, there were truncated cone-shaped stub pipes allowing the inflow of air and dye solution. Inside the reactor, 1.0 m long barrier was installed centrally. Near the effluent of the reactor there was a separator.

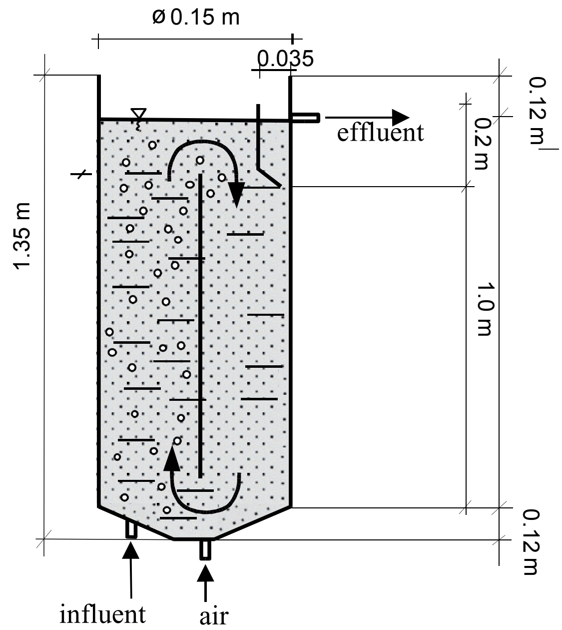

Fig. 2. Scheme of *air-lift* reactor.

Table 2. Technological assumptions of the research of Black DN adsorption by chitin in *air-lift* reactor.

Parameter		Unit	Values
Flow rate	(q)	dm^3/h	1.7, 8.5, 17
Chitin concentration	(m)	g d.w./dm^3	1, 5
Inlet dye concentration	(C_0)	mg/dm^3	10, 50, 100, 200, 300

Table 3. Technological assumptions of the research of Black DN adsorption by chitin in particular research series.

Inlet dye concentration	Chitin concentration in reactor					
	1 g/dm^3			5 g/dm^3		
	Flow rate					
	0.1 V/h	0.5 V/h	1.0 V/h	0.1 V/h	0.5 V/h	1.0 V/h
10 mg/dm^3	x	x	x	na	x	x
50 mg/dm^3	na	x	x	na	na	na
100 mg/dm^3	x	x	x	x	x	x
200 mg/dm^3	na	x	x	na	na	na
300 mg/dm^3	na	x	x	na	x	x

na – not analysed

The analyses of Black DN adsorption by modified chitin in the *air-lift* reactor were carried out at different flow rates, inlet dye concentrations and chitin concentration in the reactor. The pH of the solution was maintained at a level of 3.0.

Technological parameters of the research are presented in Table 2.

The analysis of Black DN adsorption by modified chitin was carried out as follows: chitin was transferred into the reactor filled with water of pH 3.0. Aeration was turned on at a pressure of 0.15 MPa, in order to force chitin movement in the reactor. Then, a solution with dye of a specified concentration was dosed, by means of a peristaltic pump, withat a rate of 1.7 dm^3/h, 8.5 dm^3/h and 17 dm^3/h, which corresponded to the flow rate of 0.1 V/h, 0.5 V/h and 1.0 V/h (V denotes reactor volume).

In total,19 experimental runs were made that differed in inlet dye concentration, chitin concentration in the reactor and flow rate. Technological parameters of the process in particular series are shown in Table 3.

In every series the investigations were carried out as long as dye concentration in the effluent was equal to its initial inlet concentration. For each initial inlet dye concentration and flow rate, control series without chitin were made. This enabled determination of the real time of dye staying in the reactor and the adsorption capacity of chitin under dynamic conditions.

Analytical Methods

The analysis of pH was carried out with the use of a HI 8818 pH-meter, chitin concentration as chitin dry weight according to the methodology described by Hermanowicz [13].

Deacetylation degree of chitin was analyzed according to Roberts [14].

Determination of Dye Concentration

Black DN concentration was assigned at a visual wavelength (λ = 580) at which absorbance was measured for the purpose of drafting a standardization curve and making conversion coefficient. The dye concentration was measured spectrophotometrically using a HITACHI 1200 apparatus.

Determination of Dye Concentration in the Air-lift Reactor

The efficiency of the process was calculated by measurements of decolourization. At regular time intervals (10 min), several samples were taken which were then centrifuged (10.000 rpm) for 10 min. The residual dye concentration was measured spectrophotometrically at 580 nm.

Results and Discussion

For practical purposes, it is assumed that the efficiency of dye removal in the reactor should vary from 90 to 99%, which means that dye concentration in effluent will reach from 1 to 10% of the initial concentration.

The research showed that the adsorption capacity of chitin under dynamic conditions depended on the inlet dye concentration and increased up to the maximum value (Q_{max}) with increasing concentration.

Figure 3 presents the adsorption capacity of chitin depending on the initial inlet dye concentration, at different flow rate and chitin concentration in the reactor.

The results indicate that, irrespective of dye flow rate and chitin concentration in the reactor, the lowest adsorption capacity of chitin was obtained at C_0= 10 mg/dm^3 –about (ca. 106 mg/g d.m. on average). At the concentration of C_0 = 50 mg/dm^3, the adsorption capacity was increased to about 184 mg/g d.m., and beginning from the concentration of 100 mg/dm^3 it remained at an almost constant (maximum) level. Mean adsorption capacity for all series, at Black DN concentration of 100 mg/dm^3 and higher, reached 240 mg/g d.m. This value was assumed to correspond with the maximum adsorption capacity of chitin under dynamic conditions Q_{max}.

An increase in the maximum adsorption capacity of chitin with increasing inlet dye concentration was found in all experimental series, irrespective of the flow rate and chitin concentration in the reactor (Fig. 3).

A decrease in the adsorption capacity of chitin at the concentration lower than 100 mg/dm^3 is of essential technological significance. In practice, this means that the chitin utilization at low inlet dye concentrations will decrease, which in turn will shorten the real working time of the reactor.

There were defined the best technological conditions in the *air-lift* reactor, i.e. flow rate, inlet dye concentration and chitin concentration determining the real working time of the reactor (t_k) which, corresponding with the supposed efficiency of dye removal and by assuming that the amount of dye adsorbed by chitin after time t_k will not be less than 60% of the maximum adsorption capacity of chitin under dynamic conditions – Q_{max} = 240 mg/dm^3.

The method of determining the real working time of the reactor and chitin utilization calculated as $Q(t)/Q_{max}$ at this time, is presented in Fig. 4.

Fig. 4 includes experimental data presenting the dependence of the efficiency of dye removal on time – Δt) and the ratio of the amount of dye adsorbed by chitin to the maximum adsorption capacity of chitin under dynamic conditions depending on time – $Q(t)/Q_{max}$).

Tables 4 and 5 compile the obtained Q/Q_{max} values corresponding with the assumed efficiency of dye removal, depending on technological parameters. Grey area indicates the series in which, when athe Q/Q_{max} value was equal or higher than that assumed as optimal (60%).

Data in Tab. 4 indicate that at chitin concentration in the reactor of 1 g/dm^3, assumed or higher than assumed degree of chitin utilization Q/Q_{max} was achieved only in one case, at the efficiency of 90% (flow rate q_3 = 1.7 dm^3/h, inlet dye concentration C_0 = 100 mg/dm^3). Low Q/Q_{max} values for Black DN concentration of 10 and 50 mg/dm^3, were mainly caused by the limiting effect of the initial dye concentration (C_0).

An increase in chitin concentration to 5 g/dm^3 (Tab. 5) caused the improvement of chitin utilization in all experimental series. At inlet Black DN concentration of 10 mg/dm^3 , the assumed Q/Q_{max} value equal to 60% was not received in any of the series. An increase in inlet dye concentration to C_0=100 mg/dm^3 resulted in the assumed degree of chitin utilization $Q_r/Q_{r,max}$ being obtained in almost all series (except for the efficiency η = 100% and 99% at q_1 = 17 dm^3/h). At the inlet concentration of C_0 = 300 mg/dm^3, the assumed Q/Q_{max} value was got only at η = 90%.

The working time of the reactor at the assumed efficiency of dye removal is presented in Tables 6 and 7. The elongation of working time depended on the concentration of the adsorbent in the reactor. In all experimental series, at the assumed efficiency of dye removal,

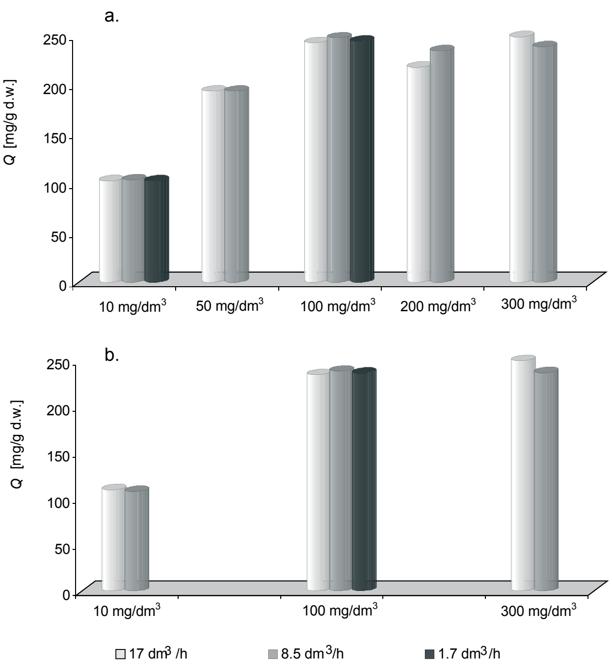

Fig. 3. Adsorption capacity of chitin at changeable inlet dye concentration and flow rate; a - chitin concentration 1 g/dm^3, b - chitin concentration 5 g/dm^3.

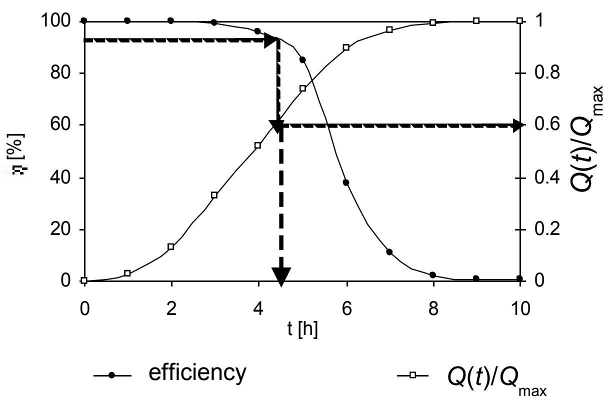

Fig. 4. Determination of real working time of reactor and adsorption capacity of chitin at assumed efficiency of dye removal.

Table. 4. Values $Q_r/Q_{r,max}$ in series differing in flow rate and efficiency of dye removal (chitin concentration in reactor 1 g/dm³).

Inlet dye concentration	Q/Q_{max} [%]											
	17dm³/h (V/h)				8.5dm³/h (0.5 V/h)				1.7dm³/h (0.1 V/h)			
	100%	99%	95%	90%	100%	99%	95%	90%	100%	99%	95%	90%
10 mg/dm³	9.8	14.6	26.8	28.7	10.9	12.6	23.1	27.9	25.2	26.4	30.4	33.9
50 mg/dm³	0	0.19	7.3	16.7	1.8	0.16	16.9	38.3	na	na	na	na
100 mg/dm³	0.4	1.81	10.6	18.8	4.9	6.47	31.0	44.3	3.2	27.2	51.9	61.1
200 mg/dm³	0	0.73	12.9	43.1	0	4.5	34.7	47.6	na	na	na	na
300 mg/dm³	0	0	4.7	18.0	0	1.1	9.8	25.9	na	na	na	na

na – not analysed

Table 5. Values $Q_r/Q_{r,max}$ in series differing in flow rate and the efficiency of dye removal (chitin concentration in reactor 5 g/dm³).

Inlet dye concentration	Q/Q_{max} [%]											
	17dm³/h (V/h)				8.5dm³/h (0.5 V/h)				1.7dm³/h (0.1 V/h)			
	100%	99%	95%	90%	100%	99%	95%	90%	100%	99%	95%	90%
10 mg/dm³	32.9	34.2	37.4	40.1	32.8	33.2	37.9	39.4		na	na	na
100 mg/dm³	0	25.1	71.9	76.2	45.0	62.6	84.4	86.6	59.4	72.6	78.0	80.3
300 mg/dm³	0	13.2	53.0	65.7	0	19.5	54.1	64.7		na	na	na

na – not analysed

Table 6 Real working time of reactor in series differing in flow rate and efficiency of dye removal (chitin concentration in reactor 1 g/dm³).

Inlet dye concentration	Working time of the reactor [h]											
	17dm³/h (V/h)				8.5dm³/h (0.5 V/h)				1.7dm³/h (0.1 V/h)			
	100%	99%	95%	90%	100%	99%	95%	90%	100%	99%	95%	90%
10 mg/dm³	3.5	4.5	7.5	8.0	7.33	9.2	13.7	14.7	71.0	71.3	83.3	92.3
50 mg/dm³	0	0	0	1.3	1.17	0.2	2.7	5.5	na	na	na	na
100 mg/dm³	0.17	0.3	0.5	1.0	0.83	1.0	2.7	3.8	4.5	15	24	27
200 mg/dm³	0	0	0	0.7	0	0	1	2.5	na	na	na	na
300 mg/dm³	0	0	0	0	0	0	0	0	na	na	na	na

na – not analysed

a 5-fold increase in the adsorbent concentration in the reactor changed extended the working time from 3.6 to 16.5-fold.

On the basis of the results of a laboratory scale research, the *air-lift* reactor was found useful for the dye adsorption onto chitin. The achieved efficiency of colour removal and a degree of chitin utilization met the assumed requirements.

Mahdavi, Talarposhti [15] in their study demonstrated the effect of different loading rates, dye concentrations and hydraulic retention times (HRTs) on colour removal efficiency under mesophilic anaerobic conditions. The colour removal efficiency was found to be affected by the loading rate of dye into the reactor, organic loading rate and hydraulic retention time. The efficiency falls as the dye loading rate increases, but rises with increased hydraulic retention time. Increased colour removal at higher organic loading rates is probably caused by improved mixing in the reactor due to a higher hydraulic throughput.

Walker [16] used granular activated carbon Filtrasorb 400 to treat effluent in a fixed-bed column system. Results of their study indicate that an increase in flow rate decreases the volume treated until breakthrough, and therefore the service time of the bed. This is due to decreased contact time between the dye

Table 7 Real working time of reactor in series differing in flow rate and the efficiency of dye removal (chitin concentration in reactor 5 g/dm^3).

Inlet dye concentration	Working time of the reactor [h]											
	17dm^3/h (V/h)				8.5dm^3/h (0.5 V/h)				1.7dm^3/h (0.1 V/h)			
	100%	99%	95%	90%	100%	99%	95%	90%	100%	99%	95%	90%
10 mg/dm^3	41.0	41	46	49.5	81.5	85	93.5	97.5	na	na	na	na
100 mg/dm^3	0.17	3.7	8.3	9.3	11.8	15.5	20.3	20.8	74.3	88.5	94.5	97.3
300 mg/dm^3	0	0.5	2.7	3.3	0	2.67	5.8	6.5	na	na	na	na

na – not analysed

and the carbon at higher flow rates; as the adsorption rate is controlled by internal diffusion, premature breakthrough occurs.

The results of our research indicate that the flow rate of dye did not influence the maximum adsorption capacity, whereas it influenced a degree of chitin utilization.

A significant effect of inlet dye concentration on the maximum adsorption capacity of chitin, a degree of its utilization and working time of the reactor was also claimed. In all experimental series, an increase in a degree of chitin utilization was observed with an increasing inlet dye concentration.

In this work, it was proved that it is possible to adjust the parameters of *air lift* reactor in order to achieve the assumed efficiency of colour removal from the solution and maximally high degree of total adsorption capacity of chitin.

Conclusions

The results obtained indicate that a degree of adsorbent utilization is an important element of adsorption design under dynamic conditions, except commonly considered, such as retention time or inlet dye concentration.

Research on the effect of technological parameters on Black DN adsorption by chitin has made it possible to determine the optimal conditions and allowed some practical conclusions to be drawn concerning the method of the exploitation of adsorption onto chitin in an *air-lift* reactor. On the basis of the investigations it can be concluded that the *air-lift* reactor is useful to dye adsorption by chitin under dynamic conditions. The results fulfilled both the criterion of the efficiency of dye removal from solution and the criterion of adsorbent utilization.

The chitin concentration in the reactor – reaching 5 g/dm^3, the flow rate of – 1.7 dm^3/h (0.1 V/h), and the inlet dye concentration of 100 mg/dm^3 were found to be the optimal parameters.

References

1. POOTS V.J.P., MCKAY G., HEALY J.J. The removal of acid dye from effluent using natural adsorbents – I. Peat. Wat. Res., **10**, 1061, **1976**.
2. POOTS V.J.P., MCKAY G., HEALY J.J. The removal of acid dye from effluent using natural adsorbents – II. Wood. Wat. Res., **10**, 1067, **1976**.
3. WALKER G.M., WEATHERLEY L.R. Adsorption of acid dyes on to granular activated carbon in fixed beds. Wat. Res., **31**, 2093, **1997**.
4. ZHANG F., KNAPP J. S., TAPLEY K. Development of bioreactor system for decolorization of Orange II using white rot fungs. Enzyme Microb. Technol. **24**, 48, **1999.**
5. RODRÍGUEZ COUTO S., DOMÍNGUEZ A., SANROMÁN A. Photocatalytic degradation of dyes in aqueous solution operating in fluidized bed reactor. Chemosphere, **46**, 83, **2002.**
6. POHORECKI R. Problemy hydrodynamiczne w inżynierii bioreaktorów. Inż. Ap. Chem. **3s**, 119, **2002.**
7. CHISTI M.Y., MOO-YOUNG M. Pneumatically agitated bioreactor devices: effects of fluid height and flow area shape on hydrodynamic and mass transfer performance. Bioreactor and biotransformation. Ed. Moody, Baker.London. **1987.**
8. CHISTI M.Y. Airlift bioreactors. Elsevier Science Publishers LTD. London. **1989**.
9. MERCHUK J.C., BERZIN I. Distribution of energy dissipation in air lift reactors. Chem. Eng. Sc. **50**(14), 2225, **1995**
10. WOJNOWSKA-BARYŁA I., BABUCHOWSKI A. Usuwanie kadmu przez ziarna alginianowe w reaktorze typu air-lift. Biotechnol., **37**, 1, **1997.**
11. MERCHUK J.C. Why use air lift reactors? TiBtech., **8**, 66, **1990.**
12. STANLEY W.I., WATTERS G.G., CHAN B. Lactase and other enzymes bound to chitin with glutaraldehyde. Biotechnol. Bioeng., **17**, 315, **1975**.
13. HERMANOWICZ W., DOŻAŃSKA W., DOJLIDO J., KOZIOROWSKI B. Fizyczno chemiczne badanie wody i ścieków. Arkady, Warszawa. **1999.**
14. ROBERTS A.A.F. Determination of the degree of N-acetylation of chitin and chitosan. [In:] Chitin Handbook. Muzzarelli R. A. A., Peter M. G. (eds), Atec Edizioni, Grottammare, Italy: pp. 127-132, **1997.**
15. MAHDAVI TALARPOSHTI A., DONNELLY T., ANDERSON G. K. Colour removal from simulated dye wastewater using a two-phase anaerobic packed bed reactor. Wat. Res. **35**(2), 425-432, **2001.**
16. WALKER G.M., WEATHERLEY L.R. Adsorption of acid dyes on to granular activated carbon in fixed beds Wat. Res., **31**(8), 2093, **1997**.