Int. J. Electrochem. Sci., 5 **(2010)** 1887 - 1897

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Laboratory Studies and Numerical Modeling of using Natural Micro beads for Environmental Applications

M. Elsayed Youssef [2], *E. A. Soliman*[1], *M. A. Abu-Saied*[1, 3], *M. S. Mohy Eldin*[1], *Salem S. Al-Deyab*[3],*El-Refaie Kenawy*[3], *A. A. Elzatahry*[1,*]

[1]Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, MuCSAT, New Boarg El-Arab City 21934, Alexandria, Egypt
[2] Computer-Based Engineering Applications Department , Informatics Research Institute, MuCSAT, New Boarg El-Arab City 21934, Alexandria, Egypt
[3] Department of chemistry, Petrochemical research chair, King Saud University, PO Box: 2455 Riyadh 11451, Riyadh, Kingdom of Saudi Arabia

[*]E-mail: aelzatahry@mucsat.sci.eg; elzatahry@gmail.com.

Received: 4 October 2010 / *Accepted*: 30 October 2010 / *Published*: 1 December 2010

Micro-beads have been prepared from naturally occurring polymers, sodium alginate (an anionic polysaccharide). Beads forming technique applied in this study is based on the principle that a laminar liquid jet is broken into equally sized droplets by a superimposed vibration. The efficiency of alginate beads for removal of methylene blue (MB) dye from effluents in dynamic batch mode has been investigated. Parameters affecting dye removal such as beads size and pH, and thus adsorption kinetics have been studied. The prepared alginate beads showed a high adsorption capacity for MB, where they removed up to 85% of the initial dye concentration throughout twenty minutes. Moreover, a mathematical model has been developed to explore mechanism removal of dye by these porous polymeric beads. The flow pattern through such porous beads has been resolved using Navier Stock equations and couple the equations of motion with mass balance equations through the multiphysics module (COMSOL).

Keywords: Alginate micro-beads, encapsulation, methylene blue, dye removal, mathematical modeling

1. INTRODUCTION

Various techniques are being used to remove pollutants from aqueous waste, where sorption is one of the most promising technologies for water purification. The most used adsorbents in this concern including clay minerals [1, 2], activated carbon [3] and polymers [4,5]. Thus, there is a growing interest in the use of bio-based materials such as polymers obtained from natural resources due to their environmental friendly properties and renewable abundance [6-8]. Alginate is a natural polysaccharide extracted from brown seaweeds. This linear polymer is composed of β-D-mannuronate (M) and α-*L*-guluronate (G) units linked by β-1, 4 and α-1, 4 glycosidic bonds. M and G units are organized in MM, GG and MG blocks, the proportion of these blocks varying with the source of the polymer. This natural polymer is one of the most extensively studied biopolymers because of being inexpensive, non-toxic and efficient for removal of pollutants from aqueous solution. Therefore, its beads are a common and well-known support material used in bioscience application for immobilization of enzymes [9] and living cells [10]. In the environmental field, alginate beads have been used for the removal of some heavy metal ions and organic pollutants [11-13].

In this work, the impact of various factors controlling the adsorption process of dye on alginate beads such as particle size, time, and pH have been investigated. In this study, the encapsulation process was used to form alginate micro-beads. This technology that developed by Inotech company is based on the principle that a laminar liquid jet is broken into equally sized droplets by a superimposed vibration. In the late 19th century, Lord Rayleigh theoretically analyzed the instability of liquid jets. He showed that the frequency for maximum instability is related to the velocity of the jet and the nozzle diameter. The optimal vibration parameters have to be determined in the light of the incorporated stroboscope. Once determined, the parameters can be reset in the future, making the process highly reproducible. Generally, by using this type of encapsulators, the bead diameter can be set in the range of 0.1 - 1.5 mm [14]. The adsorption capacity of the prepared alginate micro-beads for methylene blue has been measured, and also mathematical adsorption modelling has been studied. In earlier studies, each of film diffusion, intra-particle pore diffusion, and pore surface diffusion mechanisms have been examined individually or in a combination [15, 16].

This study aimed to study the efficiency of alginate micro-beads for removal of methylene blue dye, optimize the adsorption process, and to verify a mathematical model fitting with the results of the experimental studies.

2. EXPERIMENNTAL PART

2.1. Reagents and Chemicals

Cationic MB dye, $C_{16}H_{18}N_3SCl.3H_2O$, supplied from (NICE CHEMICALS Pvt. Ltd., COCHIN). Sodium alginate (Na-ALG) with a medium viscosity was purchased from Sigma-Aldrich Company. Calcium Chloride ($CaCl_2$) was supplied from Riedel-de Hean Company.

2.2. Apparatus and Procedure

2.3. Beads preparation

Sodium alginate solution (1.5%) was prepared by dissolving 1.5 gm of sodium alginate in 100 ml of hot distilled water with stirring until the solution become homogenous. For preparation of beads, the prepared alginate solution was injected into the encapsulator, where it has the ability to charge the surface of the beads. The voltage applied lies in the range of 400-1700V. This surface charge transforms the one-dimensional droplet chain in a funnel-like multiline stream. This will prevent beads from hitting each other during flight, or when fall into the cross-linking solution. The process has been described in Figure 1.

2.4. Dye adsorption

Aqueous dye solution was prepared by dissolving 50 mg of methylene blue in 1000 mL distilled water to obtain 50 mg L^{-1} initial dye concentrations.

Adsorption experiments were taken place using an aliquot of 100 mL MB dye solution containing 50 mg L^{-1} that was mixed with certain amount of alginate micro-beads at room temperature with mechanical stirring at 250 rpm. Samples of 0.5 mL were drawn at time interval 5 min. for 60 min. and placed in test tubes with adding 1.5 ml distilled water to be further analyzed by spectrophotometer.

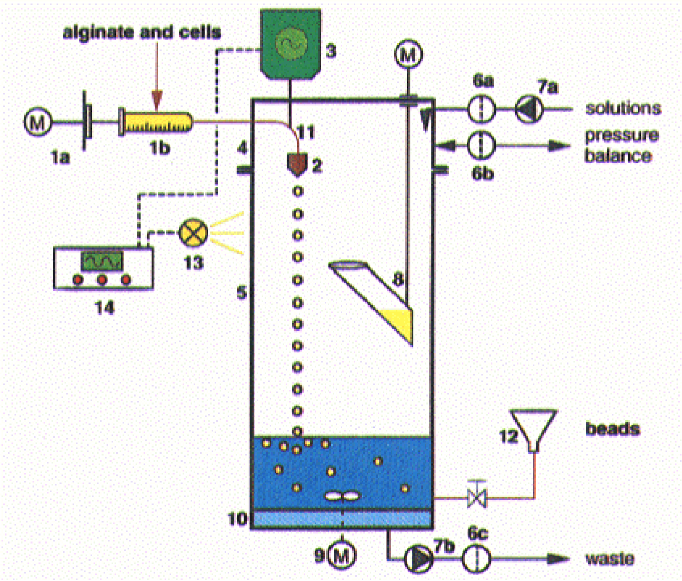

Figure 1: Schematic diagram represents the formation of alginate beads using encapsulator

The concentration of MB remaining in the supernatant after and before adsorption was determined with a 1.0 cm light path quartz cells using spectrophotometer at λ_{max} of 665 nm. Prior to the measurement, a calibration curve was obtained by using the standard MB solutions series with known concentrations.

The % dye removal is calculated for each sample according to the following relation:

$$\% \text{ dyes removal} = (1 - C/C_o) \times 100 \qquad (1)$$

Where;

C_o is the initial concentration of the dye.

C is the concentration at time (t).

To study the effect of a certain variable on the uptake of the dye, all the other variables are fixed throughout the experiments.

2.5. Beads size measurements

The particle size distribution of beads was determined by Beckman Coulter Laser Diffraction Analyzers using photon correlation spectroscopy (PCS), which determines particle size by measuring the rate of fluctuations in laser light intensity scattered by particles as they diffuse through a fluid operating at a 25 mW laser.

A constant amount of beads was dispersed in distilled water to prepare a concentration of 1% and was kept at 37 ^{o}C under agitation at 150 rpm.

3. RESULTS AND DISCUSSION

3.1. Beads size

Alginate has the ability of quick gelling on contact with $CaCl_2$ solution. The size of the formed beads depends on many factors; Nozzle diameter, charge applied to the beads surface, viscosity and concentration of the used polymeric material. In encapsulation system, the Process allows a very narrow bead size distribution. The desired diameter can be set and controlled by choosing the right nozzle diameter, mass flow and superimposed frequency.

It is well – known that the beads having small size will possess the high surface area that is associated with high adsorption capacity. For this reason, before dye removal test, the effect of factors affecting beads size distribution were examined to determine the optimum formation conditions resulting beads with smaller size and narrow size distribution. The encapsulation conditions have been settled to produce micro-beads with size average of 500 µm as shown in Figure 2.

Figure 3 illustrates the effect of beads size on the dye removal was very prominent, showing a continuous increase of removal efficiency with lowering size of the bead.

This of course related to high surface area of the beads with much smaller size and high availability of function groups, which responsible for dye adsorption over beads surface.

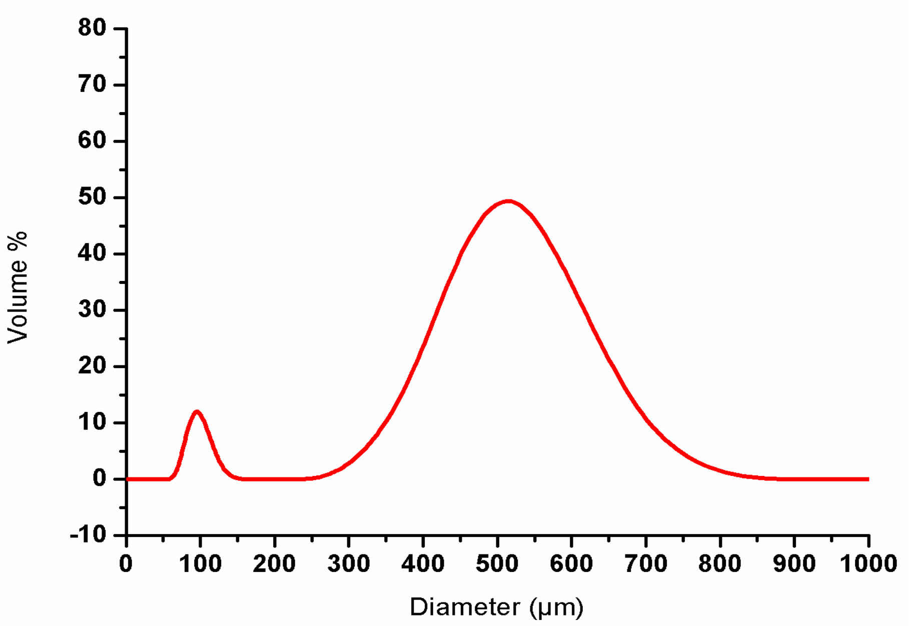

Figure 2: Size distribution of the beads

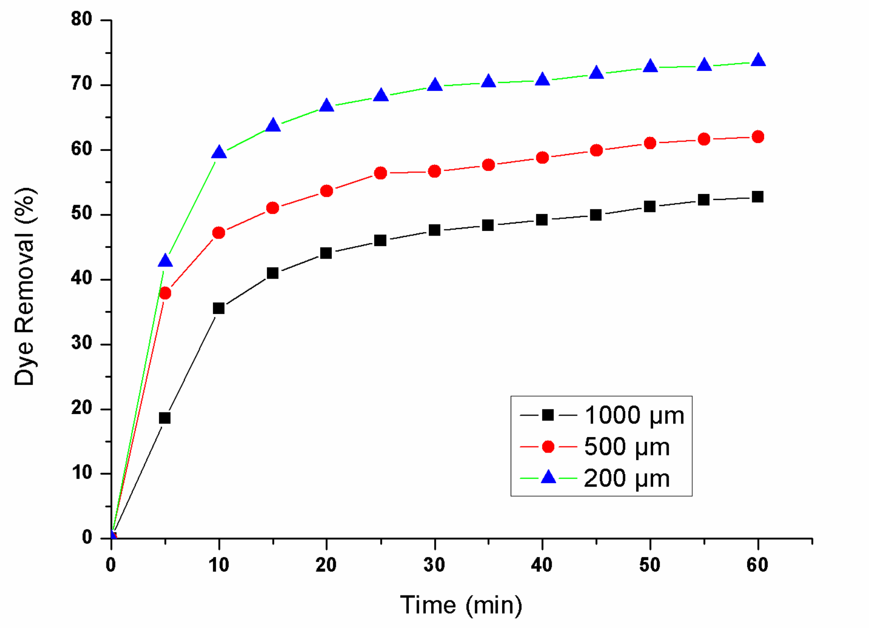

Figure 3: Effect of alginate beads size variation on dye removal

3.2. Adsorption Kinetics

Figure 4 shows the effect of contact time on the removal of MB of initial concentration (1 mmol $L^{-1)}$. Fast uptake of the dyes has been observed within the first minutes of the adsorption process. Since 50% of dye amount has been approximately removed after 15 min from the experiment start point and the equilibrium time has been measured to be 150 min of 24 h, the time setup for the experiment. The fast adsorption stage was followed by slower stage to reach its equilibrium value.

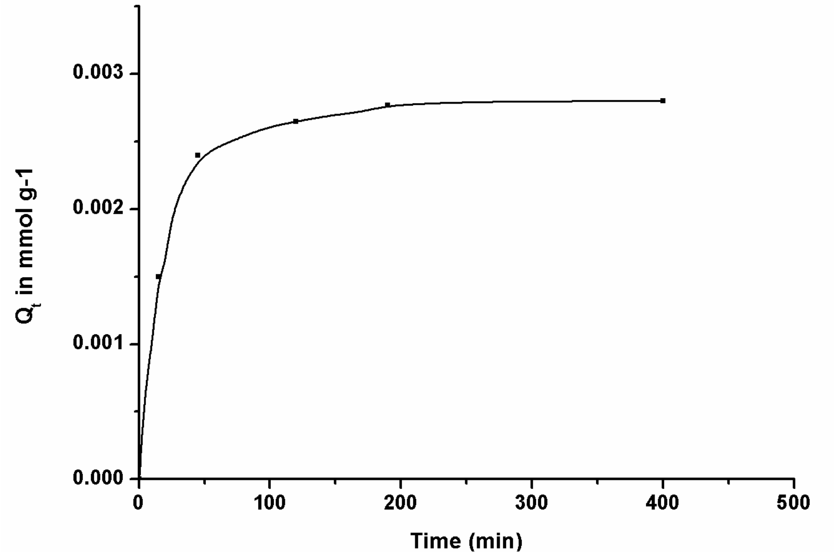

Figure 4: Adsorbed amount of MB by composite beads (Ct in mmol g-1 wet beads) as a function of time (C0=1 mmol L-1)

Several kinetic models are available to study the mechanisms of the sorption process and to fit the experimental data. Among them the pseudo-second-order equation is often successfully used to describe the kinetics of the fixation reaction of pollutants on the adsorbent.

$$\frac{dQ_t}{dt} = k(Q_{eq} - Q_t)^2 \qquad (2)$$

Where *k* (gmmol^{-1} min^{-1}) is the second-order rate constant, *Qeq* (mmol g^{-1}, wet bead) is the amount of dye adsorbed at equilibrium and *Qt* (mmol g^{-1}, wet bead) is the amount of dye adsorbed at any time *t* (min). Integrating this equation with the boundary conditions *t*=0 (*Qt* =0) to *teq* (*Qt* =*Qeq*) and then linearizing leads to

$$\frac{t}{Q_t} = \frac{1}{kQ_{eq}^2} + \frac{1}{Q_{eq}}t \qquad (3)$$

Where constant, k and *Qeq* values were calculated from the slope and intercepts of the t/Q_t versus *t* plot. A linear relationship with high correlation coefficients was observed between t/Q_t and *t*, indicating the applicability of the pseudo-second-order model to describe the sorption process. The correlation coefficients R^2, the second-order constants k and the calculated and experimental equilibrium sorption capacities Q_{eq} has been shown in Table 1.

Table 1: Adsorption kinetic constants, modelled by a pseudo-second-order equation

C_0 (mmol L^{-1})	t_{eq} (min)	$Q_{eq,exp}$ (mmol g^{-1})	$Q_{eq,calc}$ (mmol g^{-1})	k (gmmol^{-1}min^{-1})	t_{50} (min)	R^2
1	150	$2.7X10^{-3}$	$2.9X10^{-3}$	26.97	17	0.9964

3.3. Effect of pH

Figure 5 shows the effect of pH on the removal of dye by composite beads, the results shows that no apparent effect of pH on the removal of dye, this observation reflects the fact that the removal of dye is mainly due to the presence of AC which is not a pH sensitive.

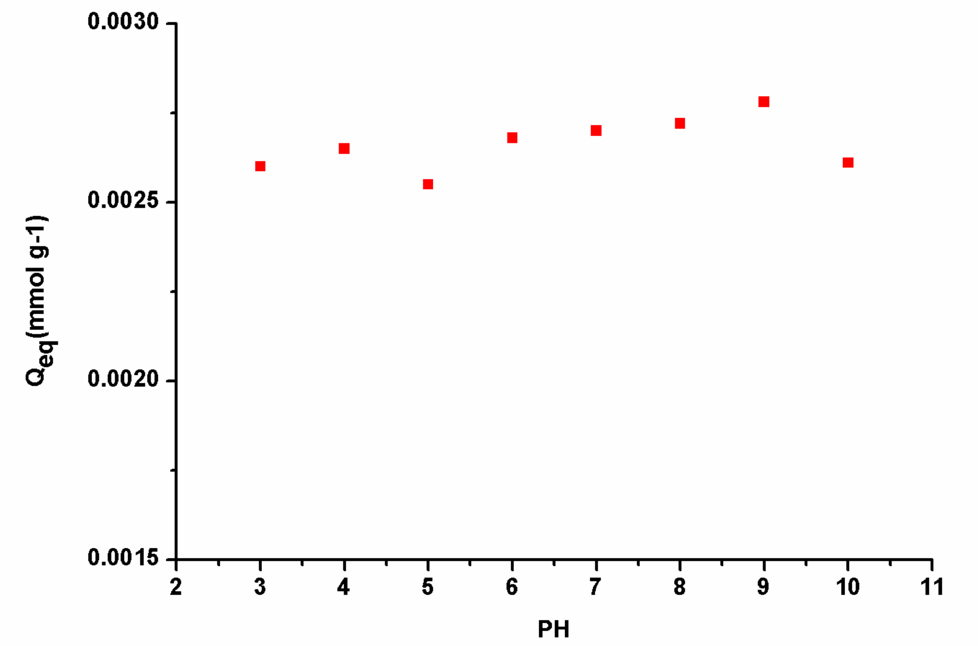

Figure 5: Effect of pH on the removal of MB dyes by composite beads (C0=1 mmol L-1)

3.4. Performance modeling and analysis

Porous particles are widely used in the chemical industry and are extensively treated in the chemical engineering. The beads are in most cases fluidized the action of gas or liquid flowing through a reactor. The fluid enters at the bottom of a bed of particles and the particles are fluidized or made to (float) by the shear force that the fluid exerts on their surface, at the same time, species dissolved in the fluid reaction on the surface and inside the porous particles.

In this study, cross-section of spherical polymer particle has been modeled. The spherical polymer particles are subjected to the dye which will be removed. The flow pattern and concentration field surrounding the spherical polymer particle and concentration field inside and outside the particle will be resolved.

3.5. Model Definition

The spherical polymer particles transposed to dye which will be removed is usually solved by assuming a uniform thick diffusion layer around the porous particle, which requires amass transfer coefficient to describe transport through the diffusion layer. The mass transfer coefficient as determined from the wall structure of the particle and transport properties of the fluid.

The flow pattern around the porous particle will be resolved using Navier Stock equations and couple the equations of motion and the mass balance equations through the multiphysics module (COMSOL)[17]. The structure of the diffusion layer will be known from the simultaneous solution of these equations.

Symmetry is assumed at the vertical boundaries, implying symmetry in the y-axis and that the modeled unit cell is typical for the system .the fluid density will be assumed constant.

The set of equation which will be used in the fluid sub domain denoted by Φ_f are

$$\mu\nabla^2 u+\rho\,(u.\nabla)u+\nabla p=0 \qquad \text{in } \Phi_{f.} \qquad (4)$$

$$\nabla u=0. \qquad \text{in } \Phi_f \qquad (5)$$

Where μ denotes the dynamic viscosity (kg/m.s), u is the velocity vector (m/s),ρ is the fluid density(kg/m^3) and p denotes pressure (pa).

The coupling of motion equation to the mass transport equation, for the reactant in he fluid at steady-state, through:

$$\nabla.\,(-D\nabla C+CU)=0. \qquad \text{in } \Phi_f \qquad (6)$$

Where D denotes the diffusion coefficient (m^2/s) and C the concentration (mol/ m^3)

The mass balance in the pellet by using an effective diffusion coefficient in the porous media is defined as following:

$$\nabla.(D^{eff}\,\nabla C)\ -KC^2)=0 \qquad \text{in } \Phi_{pl} \qquad (7)$$

Where, D^{eff} denotes the effective diffusion coefficient (m^2/s) and K the rate constant fir the second order reaction (m^3/s.mol). D^{eff} is related to the porosity and tortuosity of the pellet.

The boundary conditions of the fluid flow as following:

$u.n=u_o$ at inlet (8)

$u.n=0$ at $\delta\Phi_{fl}$ (9)

$u =(0,0)$ at $\delta\Phi_{pl.1}$ (10)

$p=0$ at $\delta\Phi_{outlet}$ (11)

Where $\delta\Phi_{pl}$ is sub domain boundary, since the Navier Stockes equation and continuity equations are not defined in the pellet domain.

The boundary conditions for the mass transport equation can be defined by assuming that the inlet concentration of the die in water is known

$C = C_o$ at $\delta\Phi_{inlet}$ (12)

$(-D\nabla C+CU).\ N = 0$ at $\delta\Phi_{f,1}$ and $\delta\Phi_{f,2}$ (13)

$(D^{eff}\ \nabla C).n = 0$ at $\delta\Phi_{pl}$ (14)

$(-D\nabla C+CU).n = Cu.n$ (15)

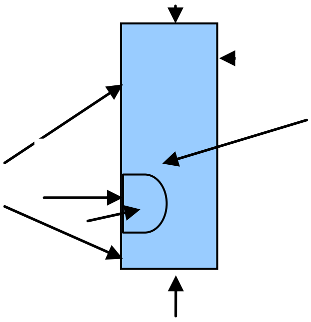

Figure 6: Schematic diagram of the domain that will be modeled.

Figure 6 shows a schematic representation of the domain that will be modeled. The dye is introduced at the bottom of the picture and exits at the top. Symmetry is assumed at the vertical boundaries, implying symmetry in the y-axis and that the modeled unit cell is typical for the system. Furthermore, It will be assumed that the density of the fluid does not change due to the sorption process on the beads.

Figure 7 shows the diffusion layer, in the free fluid surrounding the particle, is of non uniform thickness. This results in a non-symmetrical concentration distribution along the outer surface of the particle. The diffusion layer at the particle surface, facing the inlet of the dye, is far thinner than that obtained behind the particle. Moreover, depletion of the dye, along the main direction of flow, influences the concentration around the surface of the particle.

It is seen from figure 8 that the maximum velocity occurs in the contraction between the particle and the symmetry line on the right side. There are two stagnation zones in front and behind the particle.

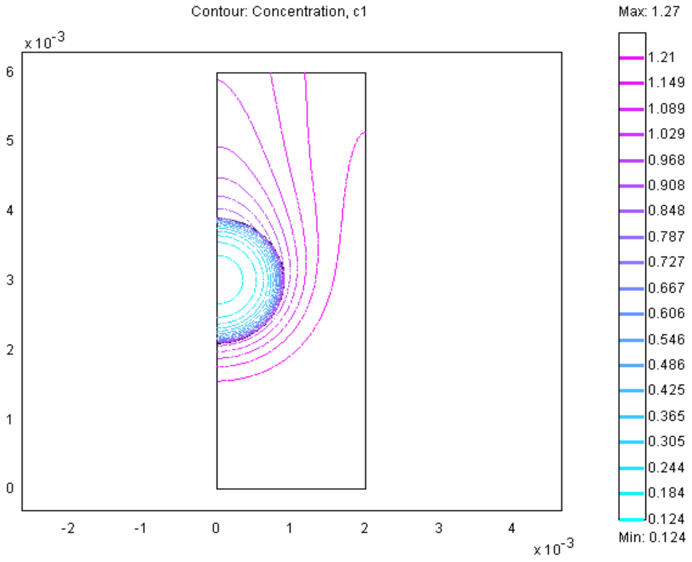

Figure 7: Contour lines of concentration

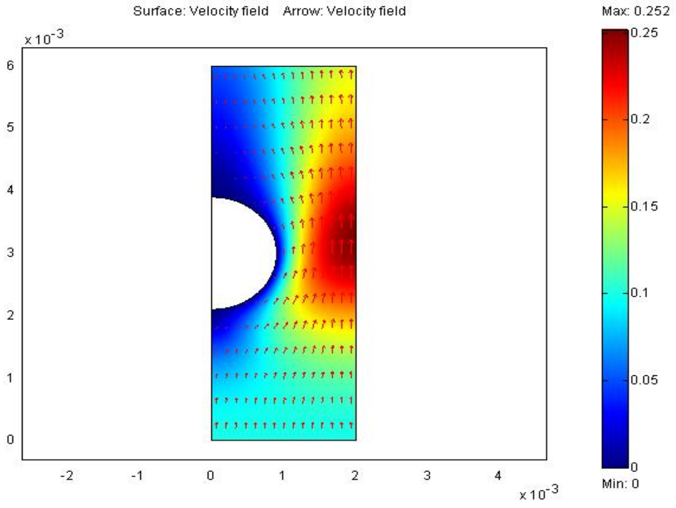

Figure 8: Flow pattern of dye around the beads

4. CONCLUSION

In the last two decades, many researches have been taken place on the removal of environmental pollutants using adsorption on various absorbents either those from agro-waste or those extracted from renewable resources such as biopolymers because of being inexpensive and efficient items in this respect. Our study has focused on forming alginate micro-beads using encapsulation technique, the prepared beads exhibited high adsorption capacity for MB where removed 85% of the dye content within twenty minutes. Significant effect has been exhibited for the size of alginate beads on adsorption capacity for MB. However, there is no significant effect has been shown for pH. Notwithstanding, little researches have been carried out on the modeling and simulation of these processes. The mathematical model developed in this study indicated that the dye removal by these micro-beads hasn’t just based on the surface adsorption, but MB dye interpenetrates the internal layers of the beads.

References

1. M. Dogan *et al.*, *Journal of Hazardous Materials* 109 (1–3) (2004), pp. 141–148.
2. P. Liu and L. Zhang, *Separation and Purification Technology* 58 (1) (2007), pp. 32–39.
3. J.M. Dias *et al.*, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review, *Journal of Environmental Management* 85 (4) (2007), pp. 833–846
4. N.K. Lazaridis *et al.*, Chitosan derivatives as biosorbents for basic dyes, *Langmuir* (2007).
5. S. Mondal, Methods of dye removal from dye house effluents. An overview, *Environmental Engineering Science* 25 (3) (2008), pp. 383–396.
6. G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Progress in Polymer Science* 30 (1) (2005), pp. 38–70.
7. G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, *Bioresource Technology* 97 (9) (2006), pp. 1061–1085.
8. F. Delval *et al.*, Preparation, characterization and sorption properties of crosslinked starch-based exchangers, *Carbohydrate Polymers* 60 (1) (2005), pp. 67–75.
9. Ribeiro, C.C., Barrias, C.C., et al., 2004. *Biomaterials* 25 (18), 4363–4373.
10. Smidsrod, O., Skjak-Brk, G., 1990. *Trends Biotechnol*. 8, 71–78.
11. Aravindhan, R., Fathima, N.N., et al., 2007. *Colloids Surf. A: Physicochem. Eng. Aspects* 299 (1–3), 232–238.
12. Nasr, M.F., El-Ola, S.M.A., et al., 2006. *Polymer-Plastics Technol. Eng.* 45 (3), 335–340.
13. Vincent Rocher, Jean-Michel Siaugue, Vale´rie Cabuil, Agne`s Bee, *Water Research* 42 (2008) 1290 – 1298.
14. INOTECH Biotechnologies Ltd, www.inotech.ch
15. Breuher, L.E., Frantz, D.C., and Kostecki, J.A., “ Combined Diffusion in Batch Adsorption Systems Displaying BET Isotherm Part II”, *American institute of chemical Engineering Symposium Series*, Vol. 63, p. 251, 1967.
16. Crittenden, J.C., “Mathematical Modeling of Absorber Dynamics-Single Components and Multi-Components”, Ph.D. Thesis, Michigan University, USA, 1976.
17. *Elzatahry,A.A., Hassan, H.M., Yousse,M.E”, Int. J. Electrochem. Sci.,* 5 (2010) 1496 - 1506