THE USE OF ADSORPTION ISOTHERMS FOR MODELLING THE NITRITE AND SULPHITE ANIONS REMOVAL FROM AQUEOUS SOLUTIONS ON A COMPOSITE MEMBRANE

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Abstract: *In this study was investigated the adsorption of nitrite and sulphite anions on a composite membrane. Initial anion concentration, pH and adsorbent dosage were investigated in this study, as well as the adsorption kinetics and isotherms for the composite membrane (10μm) used. Kinetics of adsorption was examined by means of three kinetic models, namely: pseudo-first-order, pseudo-second-order and intraparticle diffusion models and Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherms. The results obtained revealed that the adsorption isotherms fitted the data in the following order: Temkin>Langmuir>Freundlich>Dubinin-Radushkevich models. The results indicated that the composite membrane exhibited potential application for removal of nitrite and sulphite from aqueous solutions. Mathematical modelling by means of adsorption isotherms shows that the interaction of sulphite and nitrite anions with membrane surface is localized in the monolayer adsorption, meaning that the adsorbed molecules are adsorbed at definite, localized sites.*
Keywords: *adsorption, isotherm, nitrite, sulphite, mathematical modelling*

1. INTRODUCTION

The increasing levels of nitrite and sulphite anions in drinking and groundwater due to natural and anthropogenic activities has been recognized as one of the major problems worldwide [1−5]. This imposes a serious threat to human health and environmental issues. Thus, a renewed interest in the anions removal from domestic and industrial wastewaters has been greatly increased [6−9]. Moreover, technologies for anions removal from water are of great relevance in waste treatment processes, which aim to achieve efficient strategies to obtain acceptable levels for disposal of the aforesaid anions.

Adsorption studies were conducted under various experimental conditions, such as pH, contact time, initial nitrite and sulphite concentrations, temperature and the presence of competing anions. The data from the experiments were fitted with different models to identify the adsorption mechanism. The results have been thoroughly discussed which would help in the better understanding of nitrite and sulphite anions adsorption mechanism by composite membrane [10-15].

Adsorption isotherms and anion exchange modelling equilibrium are widely studied to predict the relative affinities of anions and their distribution in the adsorbent-solution system during the purification process.Thus, we use adsorption isotherms to investigate the removal of nitrite and sulphite anions from aqueous solutions by a membrane composite adsorbent through the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich adsorption isotherms. The adsorption parameters of the models are determined by nonlinear regression. The high anion - absorbing capacity of this product apparently suggests that it can be widely used in the treatment of wastewater.

2. EXPERIMENTAL

2.1.Materials

There was used one composite membranes with pore size 10 µm. The composite membranes were prepared in the laboratory of Analytical Chemistry and Environmental Engineering Department from University Politehnica Bucharest. Synthesis and characterization of these membranes has been the subject of another article [1,11]. The degree of selectivity of a membrane depends on the membrane pore size. Depending on the pore size, they can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. Membranes can also be of various thickness, with homogeneous or heterogeneous structure. Membranes can be neutral or charged, and particle transport can be active or passive.

The nitrite anion was determined according (STAS 3048/2-96 and SR ISO 6777/96) and the sulphite anion was determined according (STAS 7661/1989).

2.2. Theories of the kinetic models

Several models can be used to describe and analyze the adsorption process of a given analyte as a function of time. It should be noted that these models can describe adequately the kinetic behavior of a solute in a given substrate, but the parameters obtained from each model cannot necessarily have a coherent physical meaning because the theoretical development of these models is usually empirical. For that reason it is important to know the border conditions that describe the different kinetic models used and how the experimental factors can significantly affect the adsorption kinetics on the membrane (Ho and McKay 1998; Madden et al., 2006; Pyrzynska, 2010; Boparai et al., 2011). It is certainly feasible to select *a priori* a kinetic model that considers, as correctly as possible, the conditions under which the adsorption of some given analytes takes place, considering the characteristics of the substrate.

3. RESULTS AND DISCUSSION

3.1. Adsorption isotherms

The isotherm results were analyzed using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Temkin adsorption isotherm has been successfully used to explain the adsorption of the two anions.

Temkin Isotherm:

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The model is given by the following equation:

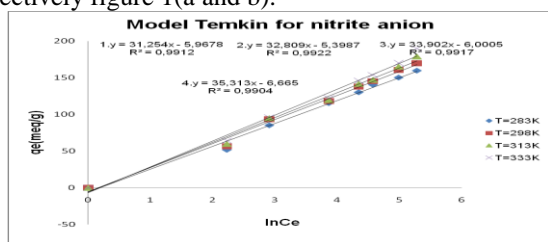$$q_e = \frac{RT}{b_T} \ln(K_T \cdot C_e) \qquad (1)$$

The linear form of Temkin equation is:

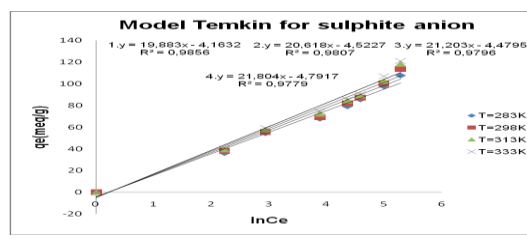$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (2)$$

where:

- b_T is the Temkin constant related to heat of sorption (J/mg)
- K_T is the binding constant corresponding to the maximum binding energy (L/g).

The Temkin constants b_T and K_T are calculated from the slope and intercept of the plot of q_e versus $ln\ C_e$ respectively figure 1(a and b).

a)   b)

The high values in this study indicates a strong interaction between adsorbate and adsorbent, supporting an ion-exchange mechanism for the present study.

Langmuir Adsorption Isotherm

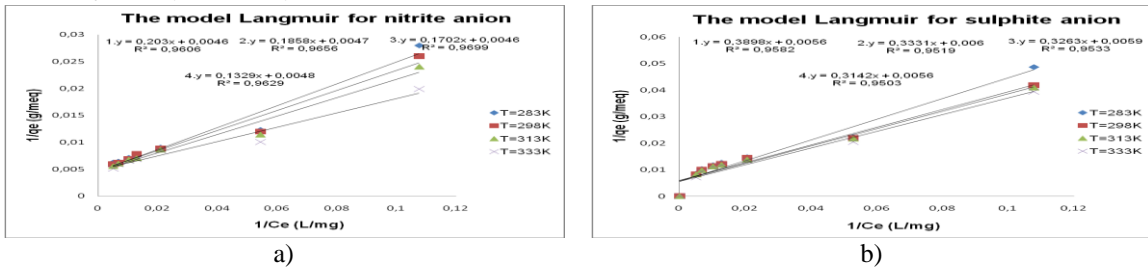The expression of the Langmuir model is given by equation:

$$q = \frac{K_L q_m Ce}{1 + K_L Ce} \tag{3}$$

where:

- q_m and K_L are the Langmuir constants, related to the adsorption capacity and energy of adsorption, respectively.

The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{Ce}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

a)   b)

Figure 2. Linear representation of Langmuir isotherm for adsorption of nitrite (a),
sulphite (b) on composite 10 µm membrane

According to the findings, the shape of the Langmuir adsorption isotherms of the nitrite anion suggests a favorable and spontaneous adsorption fig. 2(a). The Langmuir isotherms fit very well with the experimental results ($R^2 > 0.96$) presented in figure 2. The Langmuir adsorption isotherms of the sulphite are presented in fig. 2(b) and fit well with the experimental results $R^2 > 0.95$.
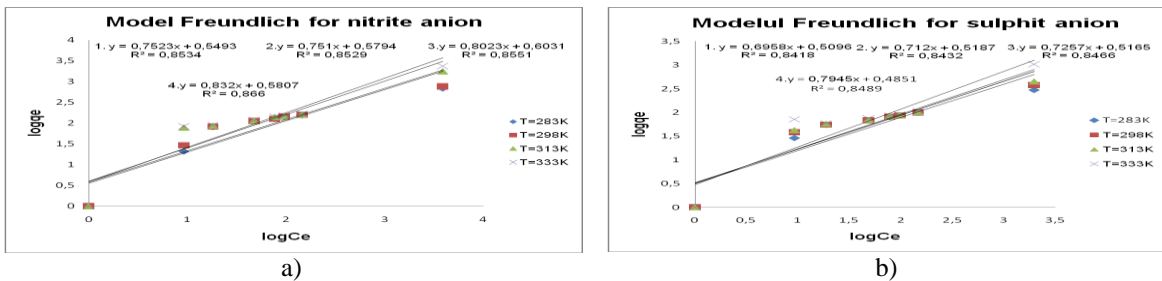
Freundlich Adsorption Isotherm:

The Freundlich isotherm is an empirical equation which estimates the adsorption intensity of the adsorbent towards the adsorbate. Freundlich equation is suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau indicates a multilayer adsorption [5,13]. The model is represented by the equation:

$$q_e = K_F \cdot C_e^{1/n} \tag{5}$$

where:

- K_F is a constant indicative of the relative adsorption capacity of the adsorbent
- n is a constant indicative of the intensity of the adsorption.

The Freundlich adsorption isotherms for nitrite and sulphite adsorption are obtained by plotting the graph of lnqe versus lnCe, as in figure 3, from which the constants of Freundlich adsorption model have been determined.

a)   b)

Figure 3. Linear representation of Freundlich isotherm for adsorption of nitrite (a),
sulphite (b) on composite 10 µm

The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases fig.3 (a and b). To determine the maximum adsorption capacity, it is necessary to operate with constant initial concentration C_0 and variable weights of adsorbent; thus ln q_e is the extrapolated value of ln q for $C=C_0$. Among the adsorption isotherm

models studied, the Freundlich model had not satisfactory correlation coefficients ($R^2 < 0.870$) for describing the adsorption of anions studied onto adsorbent.

Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$q_e = q_s \cdot \exp(-K_{ad} \cdot \varepsilon^2) \tag{6}$$

where:

- q_e, q_s, K_{ad}, are
    q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g);
    q_s = theoretical isotherm saturation capacity (mg/g);
    K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) ;
    ε = Dubinin–Radushkevich isotherm constant.

The parameter ε can be calculated as:

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{7}$$

The linear regression of the Dubinin-Radushkevich isotherm plot for the adsorption of the two anions are presented in figure 4.

| a) | b) |
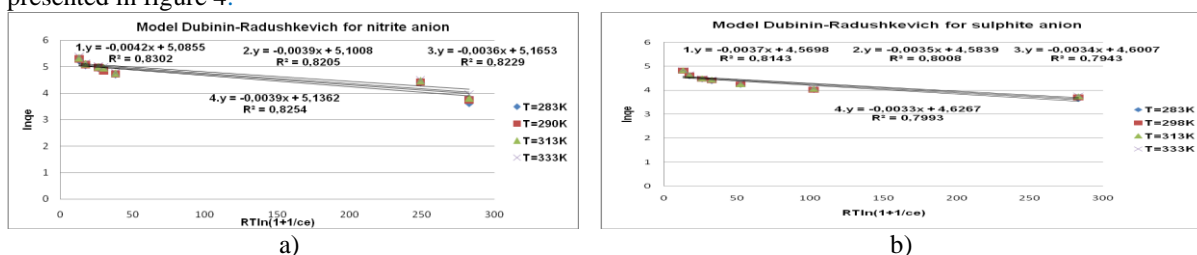
Figure 4. Linear representation of Dubinin-Radushkevich isotherm for adsorption of nitrite (a) and sulphite (b) on composite 10 μm

The values decreased with increases in temperature, thus confirming the suitability of low temperatures for adsorption. The decrease in adsorption capacity of the membrane at higher temperatures may be attributed to inactivation of the membrane surface (Dizge et al., 2009). In the range 283-333K, the experimental data fit better to the Temkin model ($0.9779 < R^2 < 0.9922$), Langmuir model ($0.9503 < R^2 < 0.9629$) than to the Freundlich ($0.719 < R^2 < 0.985$) or D-R ($0.787 < R^2 < 0.945$).

Adsorption analysis results obtained at various temperatures showed that the adsorption pattern on the composite membrane followed Temkin isotherms rather than those from Langmuir, Freundlich, and Dubinin-Radushkevich models

Kinetic adsorption

The kinetic studies predict the progress of adsorption, however, the determination of the adsorption mechanism is also important for design purposes. In order to investigate the adsorption kinetics of the anions on the adsorbent, pseudo-first order, pseudo-second order, and intra-particle diffusion models were used.

**Pseudo-first and second order models**

The kinetics of anions adsorption was studied to verify the adsorption mechanism. The first-order rate expression of Lagergren [4,12] and pseudo-second order rate [4,14] expressions were applied in this study. Lagergren suggested that a pseudo first-order rate equation for sorption of solutes from a liquid solution is represented as follows:

$$\log(q_e - q_t) = \log q_e - 1/2.303k_1 t \tag{8}$$

where:

- q_e is the adsorption capacity at the equilibrium;
- q_t is the individual capacity in a given time;
- k_1 and k_2 are the pseudo-first and pseudo-second order rate constants, respectively;
- t is the time [min].

The value of the adsorption rate constant (k_1) for nitrate adsorption by adsorbent was determined from the plot of $\log(q_e - q_t)$ against t. Although the correlation coefficient value is 0.91 for nitrate anion and 0.867 for the sulphite anion, the experimental qe value do not agree with the calculated one, obtained from the linear plot. This result indicated that the anions adsorption system do not follow a first-order reaction.
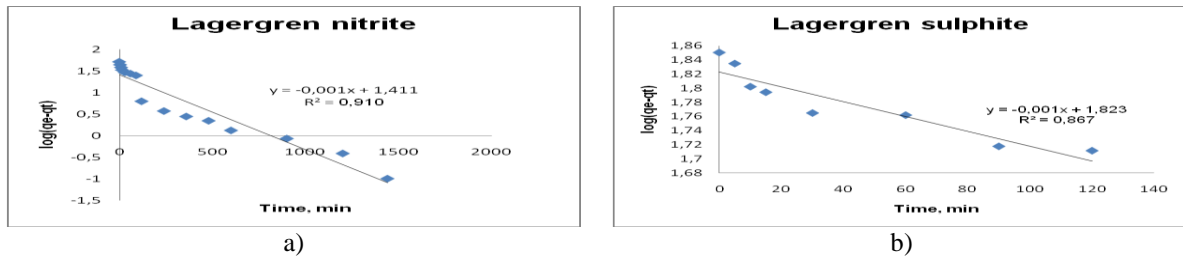
Figure 5. Linear representation of Lagergren model for adsorption of nitrite (a),
sulphite (b) on composite 10 µm

Another model for the analysis of adsorption kinetics is pseudo second-order. This model proposed by **Ho&McKay**[12,14] can be used to explain the sorption kinetics figure 5 (a and b). The model is based on the assumption that the adsorption follows a second order chemisorption. The pseudo-second order model can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where:

- k_2 is the rate constant of Ho &McKay equation (g/mg/min).

The plot of t/q versus t gives a straight line with slope of 1/q and intercept of $\dfrac{1}{k_2 q_e^2}$. There is no need to know any parameter before hand and the grams of solute adsorbed per gram of sorbent at equilibrium (q_e) and sorption rate constant (k_2) can be evaluated from the slope and intercept, respectively.
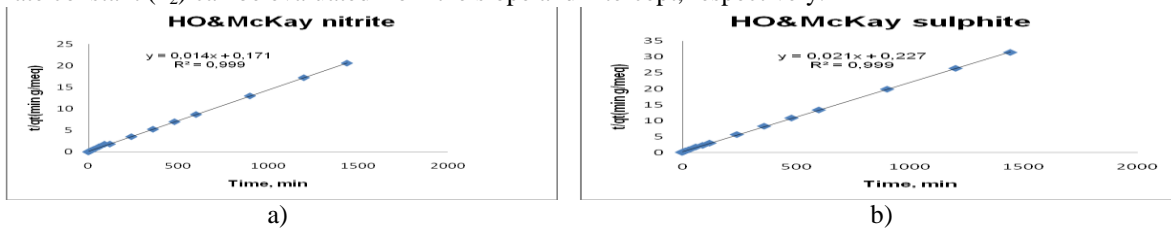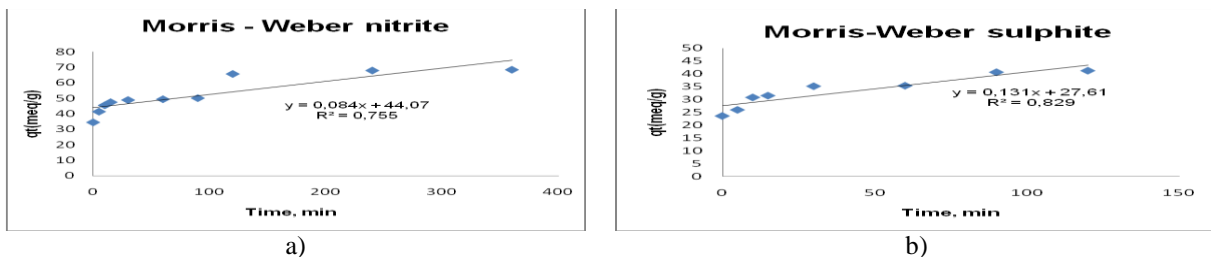

Figure 6. Linear representation of HO&McKay model for adsorption of nitrite (a),
sulphite (b) on composite 10 µm

Figure 6 shows the adsorption kinetics for pseudo second-order rate equation of nitrite, sulphite on the adsorbent. The theoretical q_t value also agreed very well with the experimental q_e value, indicating the pseudo second-order kinetics. In addition, the correlation coefficient for the second-order kinetic model was higher than 0.99 for the both anions. This suggest that the applicability of this kinetic equation and the second-order nature of the adsorption process of anions on the adsorbent are very good.

Experimental q_e values were compared with q_e value determined by pseudo-first and second-order rate kinetics model, which suggests that adsorption is not a pseudo first-order reaction and that a pseudo-second-order model can be considered.

Morris-Weber model is one of the most important models of the intra-particle diffusion. The intra-particle diffusion model is considered in two aspects: on the one hand by the membrane pore size on the other hand, by the surface diffusion occurs aqueous solutions of the two anions studied.

Figure 7. Linear representation of Morris – Weber model for adsorption of
nitrite (a) and sulphite (b) on composite 40 µm

With Morris-Weber model can be carried out and the two anion adsorption and it is the basic equation can be written as:

$$q_t = k_{id} t^{1/2} \tag{10}$$

85

where:
- k_{id} is the intra-particle diffusion rateconstant (mg g−1 min$^{1/2}$)

As shown in fig.7, the linear line do not pass through the origin and this deviation from the origin near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption. This means that the pore diffusion is not the only rate limiting mechanism in the adsorption process. It has been reported that if the intra-particle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin, which is not the case in this study. It may be concluded that surface adsorption and intra-particle diffusion are concurrently operating during the anions-adsorbent interactions.

4. CONCLUSIONS

In this work, the ability of composite membrane to remove nitrite and sulphite anions from aqueous solution was investigated. The best results obtained at various temperatures revealed that the adsorption isotherms fitted the data in the following order: Temkin > Langmuir > Freundlich > Dubinin-Radushkevich models. The composite membrane exhibited potential application for removal of nitrite and sulphite anions from aqueous solutions, at four different temperature. The most important models for intra-particle diffusion are Morris-Weber model.

The maximum adsorption capacity corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules is assumption by the Langmuir model. Adsorption seems to be a more attractive method for the removal of nitrite and sulphite in terms of cost, simplicity of design and operation.

The indirect sorbate/adsorbate interactions on adsorption isotherms has revealed that heat of adsorption of all the molecules in the layer would decrease linearly with coverage and was described by the Temkin and Pyzhev models.

References
[1] Segarceanu M., Pascu D.E., Traistaru G.A., Pascu (Neagu) M., Teodorescu S., Orbeci C., Optimization of Membrane Processes with Polysulfone/Polyaniline Composite Membranes, Revista de Chimie, 65(1), p. 8-14, 2014.
[2] Bhatnagar A., Kumar E., Sillanpää M., Fluoride removal from water by adsorption—A review, Chemical Engineering Journal, 171, p. 811–840, 2011.
[3] Dron J., Dodi A., Comparison of Adsorption Equilibrium Models for the Study of Cl^-, NO_3^- and SO_4^{2-} Removal from Aqueous Solutions by an Anion Exchange Resin, Journal of Hazardous Materials,190(1-3), p. 300–307, 2011.
[4] A. de Lima A. C., Nascimento R.F., F. de Sousa F.,Filho J. M.,Oliveira A.C., Modified coconut shell fibers: A green and economical sorbent for the removal of anions from aqueous solutions, Chemical Engineering Journal , 185– 186, p. 274– 284, 2012.
[5] Hannachi C., Guesmi F., Missaoui K., Hamrouni B., Application of adsorption models for fluoride, nitrate, and sulfate ion removal by amx membrane, International Journal of Technology 1, p.60-69, 2014.
[6] Labbez C., Fievet P., Szymczyk A.,Aoubiza B.,Vidonne A., Pagetti J., Theoretical study of the electrokinetic and electrochemical behaviors of two-layer composite membranes, Journal of Membrane Science, 184, p.79–95, 2001.
[7] Li Q, Ito K., Wu Z., Lowry C.S.,Loheide S.P., COMSOL Multiphysics: A Novel Approach to Ground Water Modeling, Ground Water, 47(4), p. 480–487, 2009.
[8] Gholipour M., Hashemipour H., Evaluation of multi-walled carbon nanotubes performance in adsorption and desorption of hexavalent chromium, Chemical Industry&Chemical Engineering Quarterly, 18(4),p.509−523, 2012.
[9] Aikpokpodion P.E., Osobamiro T., Atewolara-Odule O. C., Oduwole O. O. and Ademola S. M., Studies an adsorption mechanism and kinetics of magnesium in selected cocoa growing soilsin Nigeria, Journal of Chemical and Pharmaceutical Research, 5(6), p.128-139, 2013.

[10] Voicu S.I., Nechifor A.C., Serban B., Nechifor G., Miculescu M., Formylated polysulfone membranes for cell immobilization, Journal of Optoelectronics and Advanced Materials, 9 (11), p. 3423, 2007.

[11]Nechifor Gh., Pascu D. E., Pascu (Neagu) M., Foamete (Panait) V.-I., Membrane optimization separation process: "Study of adsorption kinetics of sulphate and nitrate ions", U.P.B. Sci. Bull., Series B, Vol. 75, p. 191-197, Iss. 4, 2013 ISSN 1454 – 2331.

[12] Ho Y. S. and McKay G., A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, Institution of Chemical Engineers Trans IChemE, 76(4), p.332-340, 1998.

[13] Benmaamar Z. and Bengueddach A., Correlation with different models for adsorption isotherms of m-xylene and toluene on zeolites, Journal of Applied Sciences in Environmental Sanitation, 2 (2),p. 43-56, 2007.

[14] Sharma I., Goyal D., Kinetic modeling:Chromium(III) removal from aqueous solution by microbial waste biomass, Journal of Scientific&Industrial Research, 68, p.640-646, 2009.

[15] Moreno L.,Crawford J. and Neretnieks I, Modelling radionuclide transport for time varying flow in a channel network, Journal of Contaminant Hydrology, 86(3–4), p.215–238, 2006.