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A Kinetics Study of *E.coli* and *S.aureus* Adsorption on Cross-Linked Hydrogels

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Abstract : Cross-linked hydrogels copolymer hydroxyl propylmethyl cellulose - acrylic acid(HPMC-co-AA) as adsorbent for two types of bacteria (*E.coli* and *S.aureus*) in aqueous solutions were studied with kinetic adsorptions. The adsorption process of *E.coli*on hydrogels was reached complete equilibrium within 90min., while the adsorption of *S.aureus* on hydrogels was reached equilibrium after 120 min.The maximum adsorption and the adsorption rate of *E.coli*on hydrogels are much higher than that of *S.aureus*. The kinetics of bacteria adsorption has been studied in terms of pseudo-first order and pseudo-second order rate expression. The results indicated that adsorption process followed two models and demonstrated that intraparticle diffusion plays a significant role in the adsorption mechanism.
Keywords: Adsorption; hydrogels; E.coli; S.aureus; Kinetics.

Introduction

Drinking water is essential to continue life, and an enough, safe and accessible supply must be available to every person. Charitable drinking water quality is a major concern worldwide in order to protect human health[1]. Bacteria are major pollutants in marine ground and even treated wastewater, include microbial and parasites causing deterioration of the surrounding medium that can present a great danger to the environment and human health[2]. Several studies have been undertaken on the pollution of bacteria and their impact on ecosystems[3]. Many methods, such as physical, chemical, and biological process of removing pollutants from wastewater, have been developed for treating bacteria containing wastewater [4,5]. Biological treatment has been shown to be very efficient for the decrease of biological and chemical organic demand, but it is ineffective for the elimination of bacteria from wastewater[6].New antibacterial treatments have been demand and studied. In adsorption process, adsorbates contained in a fluid phase diffuse to the surface of a solid, where they are chemically bound to the surface or held there by intermolecular forces[7].The most common adsorbents used for pollutants removal from wastewater are activated carbons[8,9]. Hydrogels have also been investigated as potential industrial adsorption media[10-12]. The adsorption of bacteria on activated carbon (or single-walled carbon nanotube) and natural surfaces have been pointed out and much attention has been directed towards these as a new technique for water treatment[13-16].Regarding the adsorption of bacteria using sulfide minerals surface, layered double hydroxide particles, nanostructured silicon carbide, wheat chaff and waste of molasses dates production have been described as adsorbents[13,17-19].

The aim of present work is to explore the feasibility utilizing Cross-linked hydrogels as adsorbent for bacteria. Equilibrium and kinetic analysis were conducted to investigate the mechanism of bacteria adsorption and optimization of various parameters in bacteria recovery

Materials and Methods

Instruments

Uv-visible spectrophotometer, double beam, shimadzu.pc 1650, **japan**, shaker water bath, k&k scientific, **korea,** centrifuge, 6000 rpm, cl008, **belgium**, electronic balance, sartorius lab. l420 b, ±0.0001gm, electric heat constant temperature incubator, triup international corp., **italy**, oven, triupinternational corp. **italy**, digital colony counter, k & k scientific supplier, **korea**, vortex, whirlimixer, laboratory fsa, **england**, autoclave, ls-bl00l, international corp, **italy**, hot plate with magnetic stirrer, bibbystrlintd, **uk**.

Materials:

Agar bacteriological,Eosin methylene blue agar (EMBA), Nutrient broth, Mannitol salt agar (MSA), Brain heart infusion brothwere supplied by HIMEDIA. hydroxypropylmethyl cellulose, acrylic acid, N,N-Methylene-Bisacrylamide and initier (KPS) were supplied by Fluka.

Methodology

Preparation of HPMC-co-AA

The co-polymer of HPMC co AA was prepared by solving of 0.25gm from HPMC powder to 50ml of distilled water with vigorous stirring at temperature range (60-70) °C, then it cooled at room temperature to form the HPMC solution. 0.0556mol of AA was added to 20gm of HPMC solution under constant stirring in 60°C for 20 min. then the Cross-linked (N,N-Methylene-Bisacrylamide) and initier (KPS) were added under nitrogen gas stream for 5h. The prepared co-polymer was washed by distilled water and dried at 60°C in oven. The grinding and sieving of bulky co-polymer follow that for resulting co-polymer with particle size of 150μm.

Hydrogels was washed with excessive amounts of distilled water, dried at 80°C for one hour. The hydrogels surface was used without further treatment. Wavelength of maximum absorbancy (λ_{max}) for each bacteria were selected at 550 nm. These values were utilized for estimation of quantity of bacteria adsorbed.

Enumeration of Bacteria in Stock Solution

The method of standard plate count (SPC) [13]was used to determine the number of bacteria in the stock solution. The stock solution of bacteria has been diluted by normal saline to 1 x 10^{-8} using a 10-fold serial dilution protocol. Then,0.1 mL of each dilution (1 x 10^{-2} - 1 x 10^{-8})was plated on agar plate media (Eosin methylene blue (EMBA) for *E.coli* and mannitol salt agar (MSA) for *S.aureus*). The dishes were incubated at 37°Cfor 24 h.The plates were then placed on a counting device and the number of bacterial colonies was recorded. The number of colonies recorded in stock solution of *E.coli* and *S.aureus* was found 6.0 x 10^8 and 1.7 x 10^8*cfu/mL*, respectively. The number of bacteria cells in the stock solution was also determined spectrophotometry, measured and compared with the corresponding value of McFarland standards[14].

Solutions of different concentrations for each bacteria were prepared by serial dilution. Absorbance values of these solutions were measured at the selected λ_{max}value and plotted against the concentration values. The calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Calculate the quantity adsorbed

The quantities of bacteria adsorbed were calculated according to the following equation[(22)]:-

$$Q_e or \quad \frac{x}{m} = \frac{V(C_o - C_e)}{m} \quad \text{..... (1)}$$

Where:

x : the quantity adsorbed.
m : weight of adsorbent (g).
C_o : initial concentration (mg/L).
C_e : equilibrium concentration (mg/ L).

V : volume of solution (L).

Kinetic Studies

Effect of contact time was determined by adding 0.1gm of adsorbent into 10ml bacteria solution, with initial concentration of bacterial cells $7.3\times10^7$for *E.coli* and 1.1×10^7 for *S.aureus*, was introduced into the flask and mixed, under shaking. The temperature of solution was held constant at 20^oC with a thermostatic shaker. After different time intervals, the solutions were centrifuged and volumes of 1ml supernatant were taken for spectrophotometrically measurements of bacteria content.

Results and Discussion

Adsorption rate constants of bacteria on hydrogels

To determine the equilibrium time for the maximum uptake of bacteria, the adsorption of *E.coli* and *S.aureus* on hydrogels was studied as a function of contact time, and the results are shown in Figures (1) and (2). It can be concluded that the rates of bacteria uptake on hydrogels are higher during, the initial stages and gradually decrease and become almost constant after a period of 90minfor *E.coli* and 120 min for *S.aureus*.

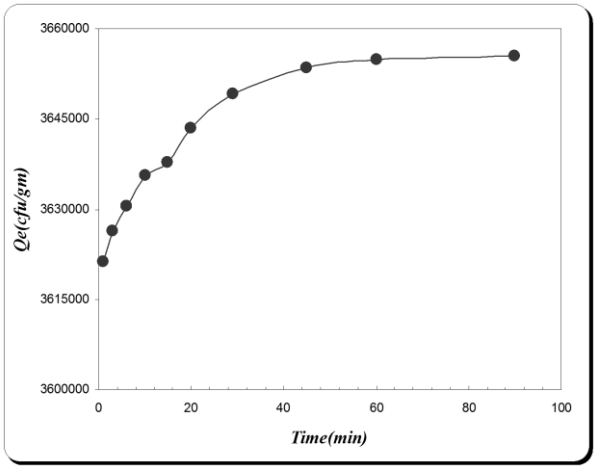


Figure (1) Adsorption kinetics of *E.coli* - hydrogels system

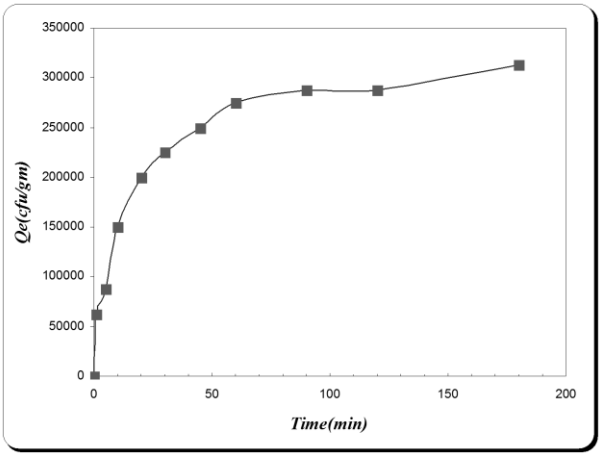


Figure (2**)Adsorption kinetics of *S.aureus*- hydrogels system**

Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data. The rate constants of the bacteria removal from the solution by hydrogels were determined using first order and pseudo-second order equations.

The lagergren first order rate equation was used to fit the experimental results. The linear form the

lagergren equation is[23]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \ldots\ldots (2)$$

Where q_e (mg/g) is the equilibrium sorption capacity and q_t (mg/g) is the amount of bacteria adsorbed at time t (min). Values of k_1 for crystal violet-hydrogels and bacteria-hydrogels systems were obtained from the slope of the plot of $ln(q_e-q_t)$vs.t (Figure (3)). The adsorption kinetic parameters from Figure (3) are indicated in Table (1).

The adsorption data were also analyzed in terms of a pseudo-second order mechanism[21,22]. The linear form of the equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad \ldots\ldots (3)$$

Where k_2 (g.mg^{-1}.min) is the rate constant of the pseudo – second order adsorption.

If the initial adsorption rate is

$h = k_2 q_e^{\,2}$

Then equation (3) becomes.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad \ldots\ldots (4)$$

by plotting t/q_t versus t (Figure (4)), a straight line could be obtained and q_e, k_2 and h can be calculated. The adsorption kinetic parameters from Figure (4) are listed in Table (1).

Table (1) Adsorption kinetic parameters of bacteria on hydrogels

	Pseudo-first order			***Pseudo-second order***			
	k_1 *(min^{-1})*	***q_e*** *(mg/g)*	***R^2***	***K_1*** *(g. .min^{-1})* mg^{-1}	***q_e*** *(mg/g)*	***R^2***	***h*** *(mg. .min^{-1})* g^{-1}
E.coli	0.0673	31382.3	0.9803	0.000009	3333333	1.0000	1×10^8
S.aureus	0.0265	219037.9	0.9656	0.0000003	333333.3	0.9656	33333.33

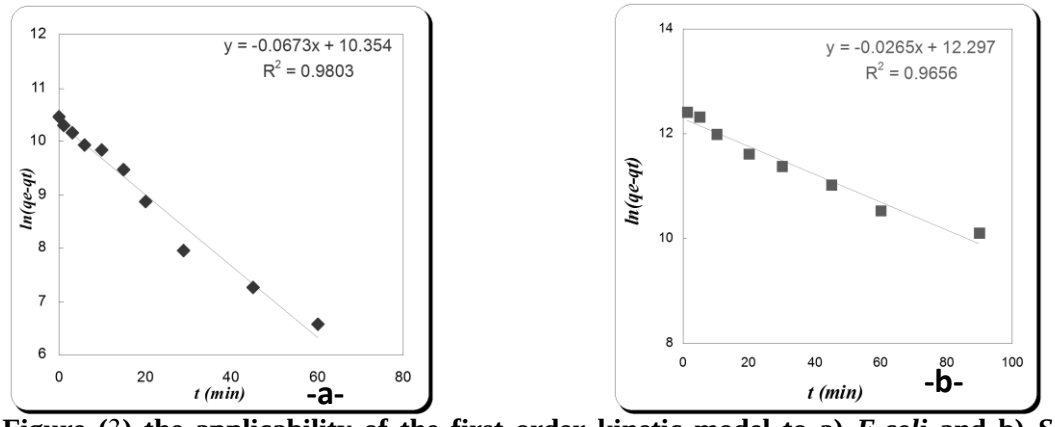


Figure (3) the applicability of the first order kinetic model to a) *E.coli* and b) *S.aureus*adsorption on hydrogels.

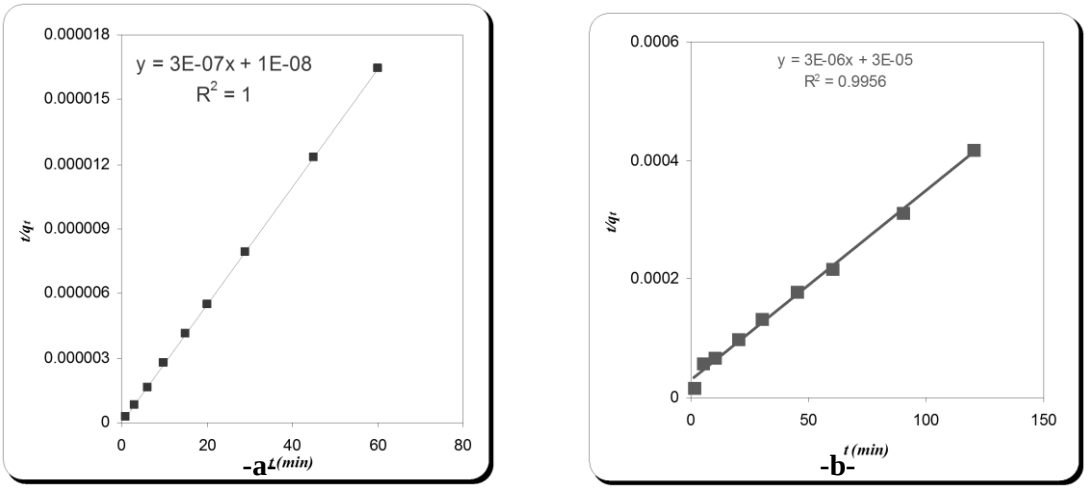


Figure (4) the applicability of the second order kinetic model to a) *E.coli* and b) *S.aureus* adsorption on hydrogels.

The applicability of the lagergren and pseudo-second order models can be examined by linear plots of $\ln(q_e-q_t)$ vs. t and t/q_t vs. t, respectively as shown in Figures (3) and (4), respectively. To quantify the applicability of each model the correlation coefficient, R^2, was calculated from these plots. The correlation coefficient, R^2, show that the pseudo-second order model fits the experimental data slightly better than the pseudo-first order. This fact indicates that the intraparticle diffusion is the rate-controlling step. The diffusion of bacteria into adsorbent was affected by its shape and size. It is generally believed that adsorption of bacteria with size less than 1µm (*S.aureus*) is higher than that with size greater than 1µm (*E.coli*) [13,24].

The mechanism of bacteria adsorption on hydrogels, which may involve the following three steps: (*i*) diffusion of bacteria molecules through the solution to the surface of adsorbent; (*ii*) adsorption of bacteriamolecules on the surface of the materials through the molecular interactions; (*iii*) diffusion of bacteria molecules from the surface into the interior of the adsorbent molecules. The second step of the adsorption of bacteria on the materials is dependent on the nature of the bacteria molecules such as anionic or cationic structures [(25)]. Due to the negatively charged characteristics of hydrogels in aqueous media, the cationic bacteria should be adsorbed more rapidly than anionic bacteria. The results obtained here indicate the effect of coulombic interactions between the adsorbent and bacteria.

In many cases, there is a possibility that intraparticle diffusion will be the rate-limiting step, which is determined by using the following equation[26]:

$$q_e = k_d\, t^{1/2} + C \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5)$$

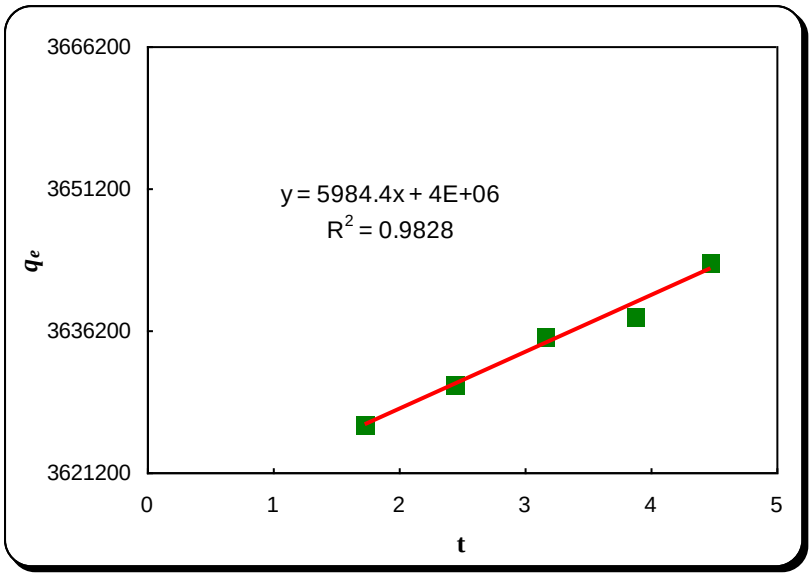
Where q_e(mg/g) is the amount adsorbed at time *t*, k_d is the intraparticle rate constant ($mg.min^{1/2}.g^{-1}$) and C is the intercept (mg/g).

The plot of q_t versus $t^{1/2}$ for adsorption of bacteria onto hydrogels is presented in Figure (5). The value of *C* (Table (2)) gives an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect[27-33]. The deviation of the straight line from the origin may be due to the difference in the rate of mass transfer during the initial and final stages of adsorption.

Table (2): The intraparticle rate constant for the adsorption of bacteria onto hydrogels

	k_d($cfu.g^{-1}.min^{-1/2}$)	Intercept	R^2
E.coli	5984.4	$4x10^6$	0.9828
S.aureus	58191.0	-92.48	0.9646

-a-



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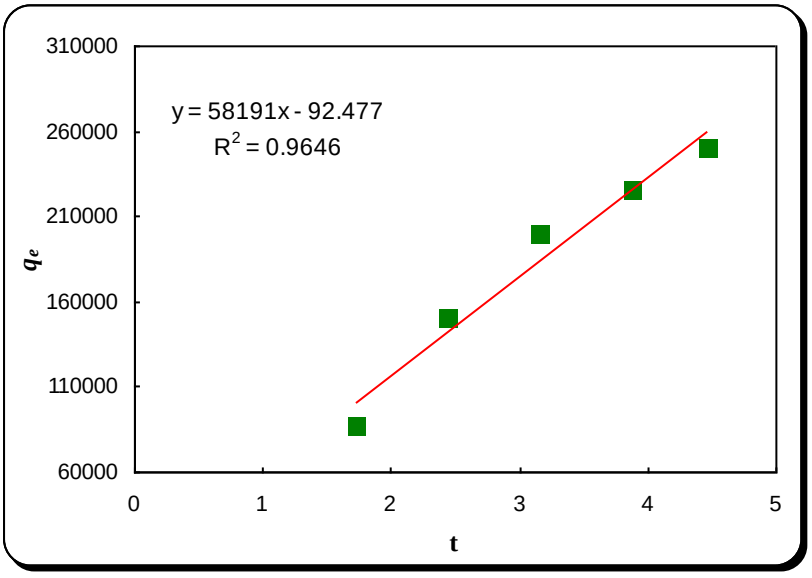

Figure (5): a) E.coli and b) S. *aureus* uptake by hydrogels according to the intraparticle diffusion model.

Conclusions:

The hydrogels could be employed as adsorbents in wastewater treatment for the removal of bacteria.The process of adsorption is relatively fast and the kinetic adsorption data fitted well to the second order kinetic model, indicating an intraparticle diffusion mechanism.

References

1. Gro-Harlem B. and Sergio V.,Guidelines for drinking-water quality, 4th ed.,World Health Organization (WHO),2003, PP:7-15.
2. Lucy A., Michael J., Juliet C. and Courtney S.,clearing the Waters: A focus on water quality solutions,UNON, Nairobi,2010, pp:50-51.
3. Meena P., Peter H., Lovett G., Tear T., Evers D., Findlay S., Cosby B., Dunscomb J., Driscoll C. and Weathers K., The Year in Ecology and Conservation Biology,2009,1162: 99–135.
4. Reife A., Othmer Encyclopedia of Chemical technology, John Wiley & sons, Inc: New York, 1993, pp: 753-784.
5. Amin M., Alazba A. and Manzoor U.," Advances in Materials Science and Engineering", Hindawi Publishing Corporation,2014, p.24.

6. Brahimi-Horn MC, Lim KK, Liang SL, Mou DG. Binding of textile azo dyes by Myrotheciumverrucaria.Journal of Industrial Microbiology. 1992; 10(1): 31-36.
7. Yamamoto O, Nakakoshi K, Sasamoto T, Nakagawa H, Miura K. Adsorption and growth inhibition of bacteria on carbon materials containing zinc oxide. Carbon. 2001; 39(11): 1643-1651.
8. Mohanty K., Thammu Naidu J., Meikap B. C. and Biswas M. N., Ind. Eng. Chem. Res., 2006, 45: 5165-5171.
9. Graham N., Chem XG. And Jayaseelan S., Water Science& Technology, 2001, 43 (2): 245-252.
10. Ju-Zhen Y. and Li-Ming Z., Bioresource Technology, 2008, 99 : 2182–2186.
11. Erdener K., Omer B. and Dursun S., European Polymer Journal, 2002, 38: 2133–2141.
12. Sema E., Yasemin I. and Dursun S., Polymer Bulletin, 2006, 57: 231–241.
13. Saja S., Abdul- Muhsen A, and Laith S., J. Chem. Chem. Eng., 2013, 7:40-49.
14. Rivera-Utrilla J, Bautista-Toledo I, Ferro-Garca MA, Moreno-Castilla C. Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. Journal of Chemical Technology and Biotechnology. 2001; 76(12): 1209-1215.
15. Alshamsi HAH, Alwan SH. Adsorptive removal of Cd(II) from aqueous solution onto beans peel powder as low cost adsorbent. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 2015; 6(6): 985-996.
16. A. M. Aljeboree, A. N. Alshirifi, and A. F. Alkaim. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. Arabian J. Chem. 2014; 10.1016/j.arabjc.2014.01.020.
17. Chun-yun J., De-zhou W., Wen-gang L., Cong H., Shu-ling G. and Yu-juan W., Transactions of Nonferrous Metals Society of China, 2008, 18(5): 1247-1252.
18. Liu J, Duan C, Zhou J, Li X, Qian G, Xu ZP. Adsorption of bacteria onto layered double hydroxide particles to form biogranule-like aggregates. Applied Clay Science. 2013; 75-76: 39-45.
19. Borkowski A, Szala M, C¦,apa T. Adsorption Studies of the Gram-Negative Bacteria onto Nanostructured Silicon Carbide. Applied Biochemistry and Biotechnology. 2014; 175(3): 1448-1459.
20. Hovis M. A., Kimball R. L. and Peterson J. C., Mathematics Exercises in Biotechnology, 2005, NSF Award, p.8.
21. Garcia L. S., Clinical Microbiology Procedures Handbook, 2ed, v1, ASM press, Washington, 2007, p. 5.14.1-5.14.4.
22. Voyutsky S., Colloid Chemistry, Mir Publishers, Moscow, 1978, pp. 91-116, 154-158.
23. Namasivayam C, Kanchana N. Waste banana pith as adsorbent for color removal from wastewaters. Chemosphere. 1992; 25(11): 1691-1705.
24. Fugelsang K. C. and Edwards C. G., "Win Microbiology Practical Applications and Procedures", 2ed., Springer Science & Business Media, New York, 2007, pp: 262-264.
25. Sun G, Xu X. Sunflower Stalks as Adsorbents for Color Removal from Textile Wastewater. Industrial & Engineering Chemistry Research. 1997; 36(3): 808-812.
26. Weter W. J., Jr. physicochemical process for water Quality control; Wiley – Interscience, New York, 1972.
27. Kannan N, Sundaram MM. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons - A comparative study. Dyes and Pigments. 2001; 51(1): 25-40.
28. Omran AR, Baiee MA, Juda SA, Salman JM, AlKaim AF. Removal of congo red dye from aqueous solution using a new adsorbent surface developed from aquatic plant (Phragmitesaustralis). International Journal of ChemTech Research. 2016; 9(4): 334-342.
29. Salman JM, Abdul-Adel E, Alkaim AF. Effect of pesticide glyphosate on some biochemical features in cyanophyta algae oscillatorialimnetica.International Journal of PharmTech Research. 2016; 9(8): 355-365.
30. Kamil AM, Mohammed HT, Alkaim AF, Hussein FH. Adsorption of Congo Red on Multiwall Carbon Nanotubes: Equilibrium Isotherm and Kinetic Studies. Int. J. Chem. Sci. 2016; 14(3): 1657-1669.
31. Kareem A, Alrazak NA, Aljebori KH, Aljeboree AM, Algboory HL, Alkaim AF. Removal of methylene blue dye from aqueous solutions by using activated carbon/ureaformaldehyde composite resin as an adsorbent.International Journal of Chemical Sciences. 2016; 14(2): 635-648.
32. Aljeboree AM, ,Alkaim, A. F., and Al-Dujaili, A. H. Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon. Desalin. Water Treat. 2015; 53(13): 3656-3667

33. Alkaim AF, Sadik Z, Mahdi DK, et al. Preparation, structure and adsorption properties of synthesized multiwall carbon nanotubes for highly effective removal of maxilon blue dye. Korean J. Chem. Eng. 2015; 32(12): 2456-2462.

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