Kinetic and Equilibrium studies of the Removal of Salicylic acid from wastewater using AC/ZnO

Hala A.Kiwaan, Elhossein A. Moawed, Samar A. Badawy, M.R.Mostafa

Abstract—.In this work, the efficiency of AC/ZnOnanoparitcles(10ZAC) for the removal of salicylic acid (SA) from wastewater was studied through anadsorption process. The effects of various parameters such as solution pH, initial SA concentration and contact time were examined. Adsorption kinetics followed Pseudo second orderand adsorption isotherms followed Langmiur.

Index Terms—AC/ZnO, Salicylic acid, removal, wastewater, isotherm, kinetic.

1 Introduction

Environmental pollution has been a real problem for the living creatures. Ground water pollution has been a serious threat, caused by industrial effluents containing dissolved polycyclic aromatic hydrocarbons (PAHs) and phenols. Phenols are naturally as well as artificially existing compounds. They are found in many industrial effluents, including cooking operations, pharmaceuticals, coal processing, refineries, plastics, wood products, as well as pesticide, paper and paint industries [1-10]. Drinking such contaminated water results in tissue erosion, protein degeneration, and paralysis of the central nervous system and also damages the kidney, liver and pancreas of human body [11, 12]. Water pollution damages the aesthetic nature of water, interference with the process of photosynthesis, destruction of the food web existing in water ecosystem [13].

Many techniques have been applied for the remediation of phenol from wastewater, such as electrochemical oxidation, adsorption by carbon fibers or activated carbon, MWCNT [14], waste materials [15], wet air oxidation, chemical coagulation , solvent extraction, membrane separation , bioremediation [16,17] and photo catalytic degradation .

Adsorption is favored by its efficiency and universally applicable , for the remediation of organic and inorganic compounds, even at low concentration. Adsorption has advantages of its relative ease of operation both in batch and continuous operation, regeneration and reusability of adsorbent[17, 18]. Adsorption by activated carbon is considered as a most potential trea-tment technique. The surface properties of activated carbon, i.e. the wide range of porosity and high surface area, ease of separation, cheap operational cost and remarkable adsorption affinity make AC (activated carbon) a versatile and favored material for various applications [19,20].

Transition metal oxide such as copper oxide (CuOandCu_2O) ,iron oxide (FeO,Fe_2O_3orFe_3O_4) and zinc oxide (ZnO) nanoparticles have special physicochemical properties which have arisen from the quatum size effect and high specific surface area [21,22]. Zinc oxide nanoparticles impregnated with activat-ed carbon is considered a non-toxic and green adsorbent .

The aim of the study was to evaluate the adsorption activity of zinc oxide loaded activated carbons (10ZAC) forsimultaneous removalof salicylic acid(SA) from aqueous solution.The removal behavior of 10ZAC was studied to optimize the conditions for the optimal removalof SA Kinetic, thermodynamics and equilibrium data was obtained.

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2 Experimental

2.1 Preparation of 10ZAC

10ZAC nanoparticles were obtained by direct controlled precipitation method as shown [19]. Aqueous solution of NH_4OH (7 mol/L) was added to a solution of $ZnSO_4.7H_2O$ (0.5 mol/L) drop wise with continuous stirring at room temperature in the presence of AC. Then, a solution of $NaHCO_3$(3 mol/L) was added under stirring to form a colloid of zinc hydroxy carbonate (ZCH) loaded on AC surface. Then the reaction mixture was heated up to 60 ^oC and stirred for 30 min. The precipitate was then filtered and washed with distilled water and ethanol. Finally, the powders were dried at 100 °C overnight, calcined at 400 ^oC for 2 h and grounded into fine particles.

2.2 Characterization

Morphology of 10ZAC was investigated using a JEOL

(JSM-6510LV, USA) scanning electron microscope.
FT-IR spectra were performed by a JASCO (FTIR-410 spectrometer) in the 4000-400 cm-1 spectral range .

The absorbance measurements were performed using a JASCO (V-630 UV-VIS Spectrophotometer, Japan). UV-Vis absorption spectra of ZnONPs was recorded in the solid state .

The crystallinity was determined using an XRD Brucker D8 diffractometer equipped with aCu Kα radiation (λ=1.5418 Å) with 40 kV voltage and 40 mA current.Surface area and Pore size were determined by BET and BJH techniques using a NOVA 3200 (USA).

2.3 Recommended procedures

The adsorption of SA onto 10ZAC was investigated using a batch experiments. 0.1 g of 10ZAC, was added to 25 mL of the SA solution, then the solution was shaken, filtered and the remaining SA concentration in solution was analyzed at λmax= 297 nm. The best condition for removal of SA can be determined by studying the effects of pH, contact time and initial SA concentration. The concentration of pollutants is measured before and after the time of shacking 0.1 g of adsorbent with SA solutions to give Co, Ce.

The percentage of dye removal (%E) and adsorption capacity (q_e) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$q_e = (C_o - C_e)\ V/m \quad (2)$$

Where, C_o is the initial SA concentration, C_e is the concentration ofSA in solution at equilibrium, V is the volume of SA solutions and m is the mass of adsorbent.

3 Results and Discussion

3.1 Optimum conditions for SA removal using 10ZAC

3.1.1 pH

The effect of the pH on the removal of SA (40 mg/L) using 10ZAC was studied (Fig.1).The removal rates of SA onto 10ZACdecreases from (98 – 94%)by increasing the pH values from 4 to 12.The maximum absorption of SA was obtained in an acidic medium pH < 4.

3.1.2 Contact time

The effect of contact time on SA(100 mg/L) removal using 10ZAC was investigated at pH=3.5 (Fig. 2).The removal rates of SA were initially rapid, where 59%-71% of the total amount SA was removed within 25 min. Then the rates become slower with increase in time until reaching 81% of the dark and light at 90 min.

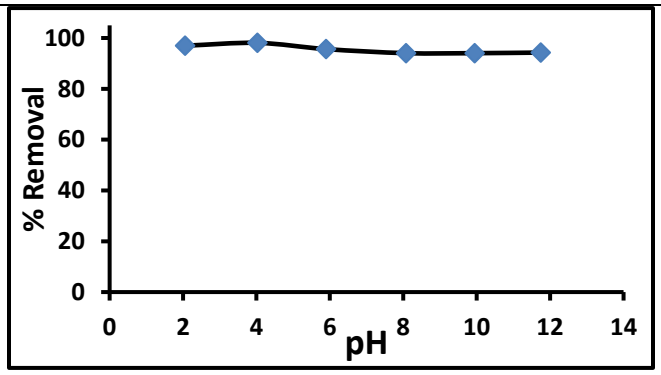

Fig.1 Effect of pH on MB removal using ZnONPs in dark and light

3.1.3 Initial SA concentration

The effect of initial SA concentration was studied for different SA concentrations at pH=3.5.(Fig. 3).The removal rates of SA using10ZAC increased with increase in SA concentration within a range from 20 to 160 mg/L. The maximum adsorption capacity of 10ZAC is found 30 mg/g.

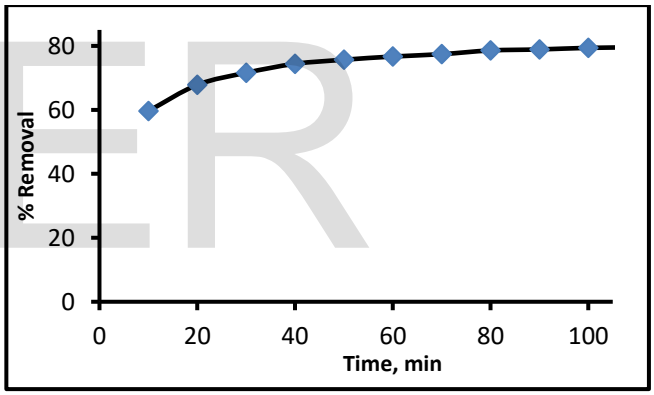

Fig.2 Effect of time on SA removal using 10ZAC at pH=3.5

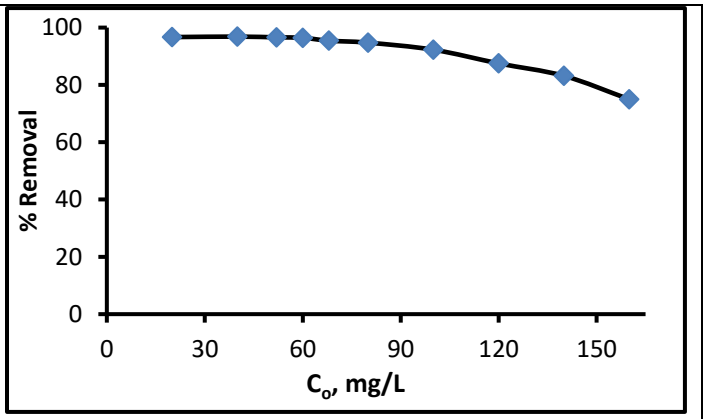

Fig.3 Effect of initial SA concentration on SA removal using 10ZACat pH=3.5

3.2 Kinetic studies

. The pseudo first-order (3)andpseudo second-order (4)were used to investigate the mechanism of adsorption and the rate controlling steps involved in the sorption.

$$\log(q_e - q_t) = \log q_e - (K_1 t/2.303) \quad (3)$$

$$t/q_t = (1/K_2 q_e^2) + t/q_e \quad (4)$$

Where $q_e$and $q_t$is the sorption capacity at equilibrium and at time t. K_1 and $K_2$is the pseudo first rate constant and the pseudo second order rate constant.The half-life times ($t^{1/2}$) of Pseudo first order are calculated by $t_{1/2} = 0.693/K_1$, while that of second order are calculated by$t^{1/2} = 1/q_e K_2$.

The data showed that the R^2 of the Pseudo second order is higher than that of the first order (Table 1). Also, higher rate constant and faster half-life timesuggests that the adsorption isfollowed Pseudo second order which controlled by chemisorption mechanismand depended on both SA and 10ZAC [25].

Kinetic modeling of the experimental data allows us to gain insight into the potential rate-controlling steps involved in the adsorption process. Tow kinetic models (i.e., Pseudo first order [$\log(q_e-q_t) = \log q_e - (k_1\ t/2.303)$] and Pseudo second order[$t/q_t = (1/K_t q_e^2) + (t/q_e)$] models) were tested to fit the experimental data for the adsorption of SA onto 10ZAC.

The diffusion mechanism was investigated using the Morris-Weber [$q_t = K_i\sqrt{t}$] , Reichenberg [Bt = -0.4977 – ln(1-F)] and [$F = (6/R)(D_i t/\pi)^{1/2}$] equations. Where q_t is the amount of SA adsorbed at time t, K_i is the intraparticale diffusion rate constant (mg/g $min^{1/2}$), C_o is the initial concentration of SA in solution , V is the volume of the SA solution and m is the mass of 10ZAC. The Bt value is a mathematical function of $F = q_t/q_e$. Di is the effective diffusion coefficient and α and K_o are constant.

A plot of q_t as a function of $t^{1/2}$ should be a straight line (R^2 = 0.936) that does not pass through the origin. The diffusion rate of SA is rapid in the initial stages and decreases with the passage of time. The average values of K_i for SA adsorption were 1.979 mg/g min^{-1}.

The relationship between Bt and t for SA adsorption was investigated, which indicates that a particular film formed along with an intraparticale diffusion. The slope of the linear plots of F as a function of $t^{1/2}$ provide the numerical value of the effective diffusion coefficient (D_i). The value of D_i for the SA adsorption was $1.5x10^{-8}$ cm^2/min.The film diffusion rate depended on the size of phenols.

Table 1
The Kinetic parameters for removing of SAusing 10ZAC

Method	*Pseudo first order*			*Pseudo second order*		
	R^2	k_1 (min^{-1})	$t^{1/2}$ (min)	R^2	k_2 (g/mg min)	$t^{1/2}$ (min)
pH 3.5	0.942	0.016	43	0.999	0.002	4.4

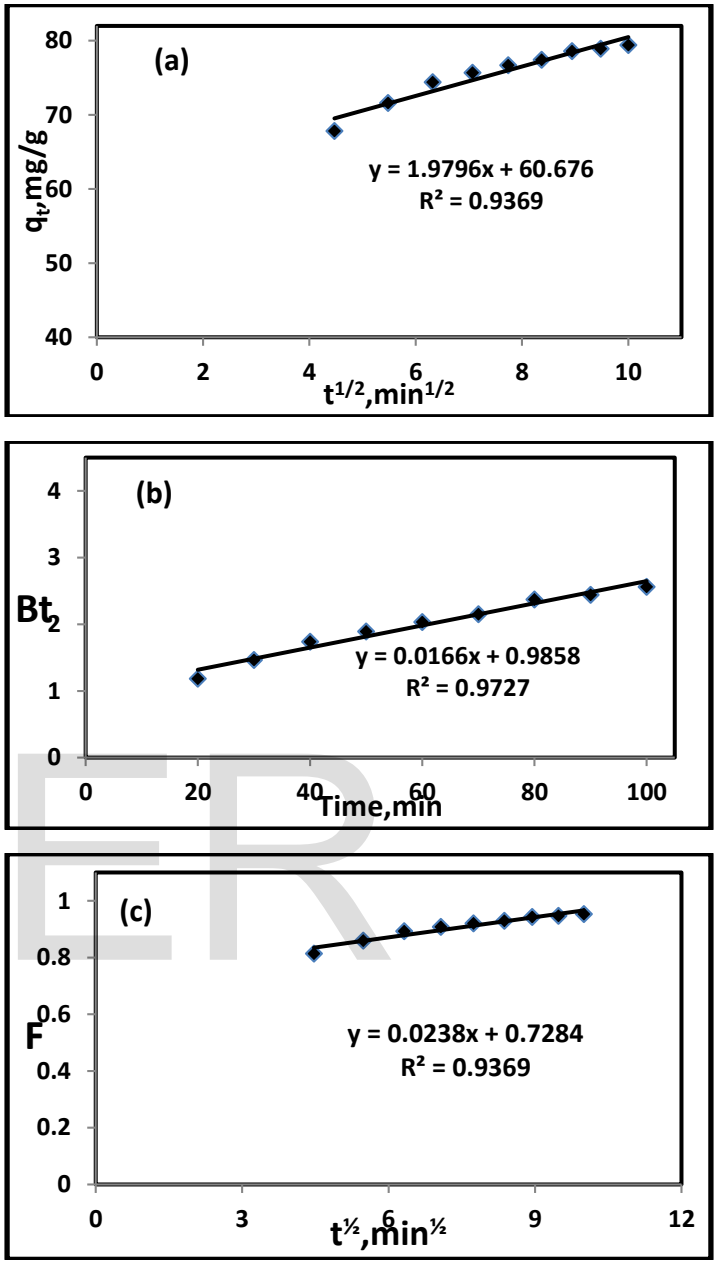

Fig.5: Diffusion models of SA removal using 10ZAC (a)Weber-Morris kinetics (b)Reichenberg diffusion (c)Boyed diffusion

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3.3 Equilibrium studies

Langmuir(5) and Freundlich (6) isotherms were applied to studythe removal behavior SAusing10ZAC.

$$C_e/q_c = (1/K_L b) + (C_e/K_L) \quad (5)$$

$$Log\ q_c = Log\ K_F + 1/n\ Log\ C_e \quad (6)$$

Where q_c is the amount of dyes adsorbed at equilibrium and $C_e$is the SA concentration at equilibrium. K_L and b are Langmuir constants, while K_F and n are Freundlich constants.

The results showed that the R^2 of Langmuir is higher than that ofFreundlich (Table 2).Suggesting for monolayer adsorption

over heterogeneous surfaces.Also, the values of 1/n are less than 1, referring to a favorable chemisorption process(Fig. 4)[25].

The linear plot of $\ln q_e$ as a function of ε^2 (Dubinin-Radushkevich isotherm ($\ln q_e = \ln K_{D-R} - \beta\varepsilon^2$) and $E = 1/\sqrt{2\beta}$, $R^2 = 0.92$) is shown in figure 7 . K_{D-R} is the maximum amount of SA adsorbed onto 10ZAC , β is a constant related to the transfer energy of the SA from the bulk solution to the 10ZAC , and ε is the Polanyi potential. Values of K_{D-R} and β were calculated as 22.78 mg/g and 0.475 mol^2/KJ^2, respectively. The adsorption energy E was determined to be 1.02 KJ/mol for SA. This result showed that the removal of SAonto 10ZAC was the adsorption mechanism (Fig. 5).

Table 2
The equilibrium parameters for removing of SAusing 10ZACat pH=3.5

Method	*Langmuir*		*Freundlich*	
	R^2	b ($L\ mg^{-1}$)	R^2	1/n
pH=3.5	0.999	0.34	0.930	0.313

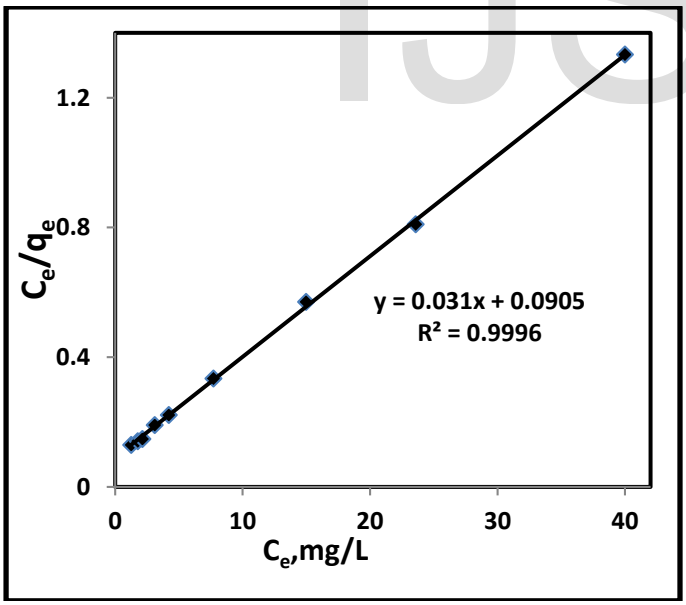

Fig.4Langmuir isotherm of SA removal using 10ZAC

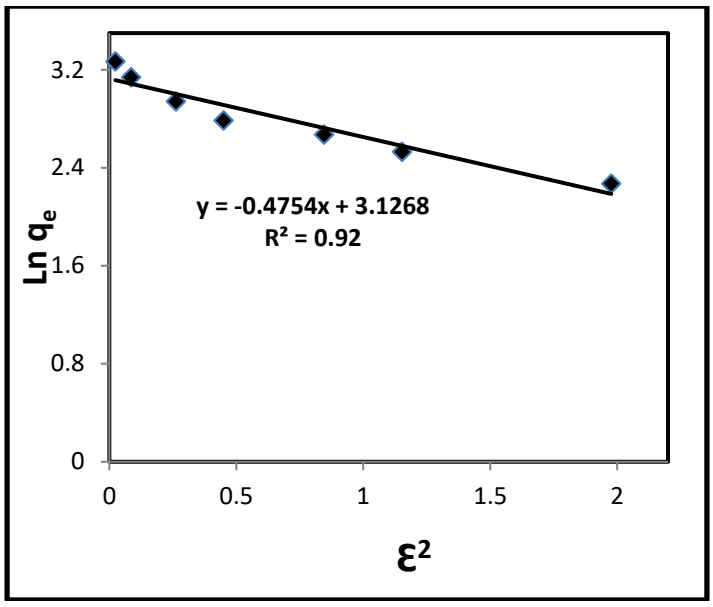

Fig. 5: Dubinin- Radushkevich isotherm of SA removal using 10ZAC

4. Conclusion

10ZAC was successfully prepared as identified by SEM, XRD, BET, FTIR and UV-Vis spectroscopy.10ZAC was tested for the removal of salicylic acid (SA) at pH=3.5. The maximum adsorption capacities of 10ZAC are found 30 mg/g within 25min over a wide pH range (2-12). The kinetic studies were followed by pseudo-second-order model.The equilibrium isotherms showed that Langmuir model were having a good fit to the experimental data. Thermodynamic parameters demonstrate the spontaneous and the exothermic nature of adsorption process. 10ZAC proved its efficiency in the removal of salicylic acid from wastewater under optimum conditions.

References

[1] E.A. Moawed, M.A. El-Hagrasy, A.A.M. Farhat, Application of the magnetic isothiouronium polyurethane sorbent for removal of acidic and basic dyes from wastewater, Journal of Cleaner Production, 2017, 157, 232–242

[2] E.A. Moawed, H.A. Kiwaan, M.M. Elshazly, Application of polyurethane@salvadora persica composite for detection and removal of acidic and basic dyes from wastewater, Journal of the Taiwan Institute of Chemical Engineers, 2017, 80, 894–900

[3] E.A. Moawed, A.E. Wahba, R.A. Gabr, Synthesis and application of LGB/St/Al2O3 biocomposite for sensitive detection and efficient removal of brilliant green dye from wastewater, Journal of Environmental Chemical Engineering 2018, 6, 7225–7232

[4] E.A. Moawed, M.A. El-Hagrasy, A.E.A. Senan, Application of bio alkyd resin for the removal of crystal violet and methylene blue dyes from wastewater, International Journal of Environmental Science and Technology, 2019, 16 (12), 8495–8504

[5] E.A. Moawed, M.A. El-Hagrasy, M. Kamal, Detection and removing of lead from wastewater using chemical treatment of polyurethane foam waste: Batch and column experiments, Desalination and Water Treatment, 2019, 159, 338–345

[6] E.A. Moawed, Hala A. Kiwaan, Amira A.A. Elbaraay, Synthesis and characterization of novel friendly biosorbents and it uses for removal of crystal violet dye from wastewater, International Journal of Scientific & Engineering Research 2019, 10(4), 1259-1278

[7] E.A. Moawed, T.A. Hegajy, T.R. Kosbar, M.S. Eissa, Removal of methylene blue dye from wastewater using ZnONPs in the dark and light, International Journal of Scientific & Engineering Research 2019, 10(7), 249-253

[8] E.A. Moawed, Hala A. Kiwaan, Amira A.A. Elbaraay, Application of cellulose, lignin and camphor stem as new biosorbents for removal of brilliant green and crystal violet dyes from wastewater, Arab Journal of Basic and Applied Sciences 2019, 26(1), 414–423

[9] Moawed, E. A. and El-Shahat, M. F., "Equilibrium, kinetic and thermodynamic studies of the removal of triphenyl methane dyes from wastewater using iodopolyurethane powder", J. Taibah. Univ. Sci., 10(1), (2016): 46-55.

[10] L. Damjanovi_c, V. Raki_c, V. Rac, D. Sto_si_c, A. Auroux, The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents, J. Hazard Mater. 184 (2010) 477–484.

[11] D. Tiwari, W. Kim, M. Kim, S.K. Prasad, S.M. Lee, Organo-modified sericite in the remediation of phenol-contaminated waters, Desalin. Wat. Treat. 53 (2015) 446–451..

[12] D. Tiwari, W. Kim, M. Kim, S.K. Prasad, S.M. Lee, Organo-modified sericite in the remediation of phenol-contaminated waters, Desalin. Wat. Treat. 53 (2015) 446–451.

[13] A. Fortuny, J. Font, A. Fabregat, Wet air oxidation of phenol using active carbon as catalyst, Appl. Catal. B Environ. 19 (1998) 165–173.

[14] Mittal, J. Mittal, A. Malviya, V.K. Gupta, Adsorptive removal of hazardous anionic dye Congo red" from wastewater using waste materials and recovery by desorption, J. Colloid Interface Sci. 340 (2009) 16–26..

[15] Z. Guo, R. Ma, G. Li, Degradation of phenol by nanomaterial TiO2 in wastewater,Chem. Eng. J. 119 (2006) 55–59

[16] G.G. Stavropoulos, P. Samaras, P.G. Sakellaropoulos, Effect of activated carbons modification on porosity, surface structure and phenol adsorption, J. Hazard Mater .151 (2008) 414–421.

[17] MA,SalehTA,DrmoshQA.Synthesis of nickel oxide nanoparticles using pulsed laserablation in liquid sandtheir optical characterization .ApplSurfSci 2012;258::6982–6.

[18] Xiong, G., Pal, U., Serrano, J. G., Ucer, K. B., and Williams, R. T.," Photoluminesence and FTIR study of ZnO nanoparticles: the impurity and defect perspective", Phys. Status Solidi C, 3(10), (2006): 3577-3581.

[19] Ghorbani, H. R., Mehr, F. P., Pazoki, H., and Rahmani, B. M. "Synthesis of ZnO nanoparticles by precipitation method", OJC, 31(2),(2015): 1219-1221.

[20] Hamedani, N. F., and Farzaneh, F, "Synthesis of ZnO nanocrystals with hexagonal (Wurtzite) structure in water using microwave irradiation",J. Sci. I. R. Iran, 17(3), (2006): 231-234..

[21] Moazzen, M., Borghei, S. M. and TaleshiF.,"Synthesis and Characterization of Nano-Sized Hexagonal and Spherical Nanoparticles of Zinc Oxide", J. Nanostruct., 2(3), (2012): 295-300.

[22] Fatehah, M. O., Aziz, H. A., and Stoll, S. "Stability of ZnO nanoparticles in solution. Influence of pH, dissolution, aggregation and disaggregation effects", J. Colloid Sci. Biotechnol., 3(1), (2014): 75-84.

[23] Meroufel, B., Benali, O., Benyahia, M., Benmoussa, Y., and Zenasni, M. A,"Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin: Characteristics, isotherm, kinetic and thermodynamic studies", J. Mater. Environ. Sci., 4(3), (2013): 482-49.

[24] Erhayem, M., Al-Tohami, F., Mohamed, R. andAhmida, K., "Isotherm, kinetic and thermodynamic studies for the sorption of mercury (II) onto activated carbon from Rosmarinusofficinalis leaves", Am. J.Anal. Chem.6(1), (2015): 1.

[25] Aljeboree, A. M., Alshirifi, A. N. andAlkaim, A. F., "Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon", Arab. J. chem., 10, (2017):S3381-S3393.