Kinetic and Equilibrium Study of Benzene Removal by Granular Dead Activated Sludge

[1]Mudhaffer S. Al-Zuhairy, [2]Ali H. Al-Aboodi and [3]Risalah A. Mohammed
[1]Southern Technical University (STU), Basrah, Iraq
[2]Department of Civil Engineering, College of Engineering, Basrah, Iraq
[3]Department of Environmental Engineering, College of Engineering Technical, Basrah, Iraq

Abstract: Benzene is one of the biggest challenges of groundwater pollution due to of its toxicity, motility in the environment and solubility in groundwater. Granular Dead Activated Sludge (GDAS) was investigated as low-cost and locally available as sorbent material for removing benzene from aqueous solution. The experimental results show that the removal efficiency has improved with increasing both of GDAS amount and the time of contact and decreasing the initial concentration of contaminant. Langmuir and Freundlich isotherm model give a good fitting for sorption process with high determination coefficient >0.998. The parameter of this model shows a favorable sorption for removing benzene by GDAS. Intra-particle diffusion model data fitting shows two separate regions, the first severe portion attributed to the immediate sorption step and another portion is the intraparticle diffusion rate is dominated. The parameters of model illustrate the external mass transport mechanisms must be considered with intra-particle diffusion.

Key words: Benzene, GDAS, sorption, isotherm model, kinetics model, mechanism of removal

INTRODUCTION

Benzene is one of the most challenges for groundwater pollution due to its toxicity, motility in the environment and solubility in groundwater (Youngren *et al.*, 1994). The International Agency for Research on Cancer (IARC) has determined that benzene is carcinogenic to humans (IARC., 1989).

Remediation of groundwater is the procedure which used to eliminate contamination from groundwater. There are numerous way to confiscate contamination. This method can be approximately divided into two groups. "Permeable Reactive Barrier (PRB) which is an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provides a flow path through the reactive media and transform the contaminants into environmentally acceptable forms to attain remediation concentration goals down gradient of barrier" (Simantiraki *et al.*, 2013). The main engineering challenge is determination of appropriate type and amounts of reactive materials in a permeable wall and proper placement techniques. The availability and the cost are important criteria for selecting a reactive material. Therefore, the target of this study was to conduct batch test investigations on low-cost, locally and readily available materials, Granular Dead Activated Sludge (GDAS) to be used as a reactive material in a PRB.

MATERIALS AND METHODS

Sorbent and sorbate: Granular Dead Activated Sludge (GDAS) was collected about 25 cm depth of dried bed in Hamdaan municipal treatment plant, Basrah/South of Iraq. This slurry was air-dried for seven days and then, sieved into (2.36-0.075) mm diameter mesh. However, this fraction was repeatedly washed in distilled water and dried at 70°C for 6 h prior to use. Energy-Dispersive X-ray Spectroscopy (EDS) is used for analysis of GDAS, the percentage of chemical inorganic component for selected section of reactive media is shown in Table 1 and Fig. 1.

Scanning Electron Microscopy (SEM) has been used to assess the characteristics of the surface morphology and surface physical properties for the sorbent

Table 1: Percentage for chemical composition of GDAS by EDS test

Element	Atomic concentration (%)
Carbon	76.05
Oxygen	21.99
Bromine	0.21
Silicon	0.50
Aluminum	0.75
Calcium	0.20
Copper	0.05
Magnesium	0.11
Sulfur	0.01
Potassium	0.01
Iron	0.12

Corresponding Author: Mudhaffer S. Al-Zuhairy, Southern Technical University (STU), Basrah, Iraq
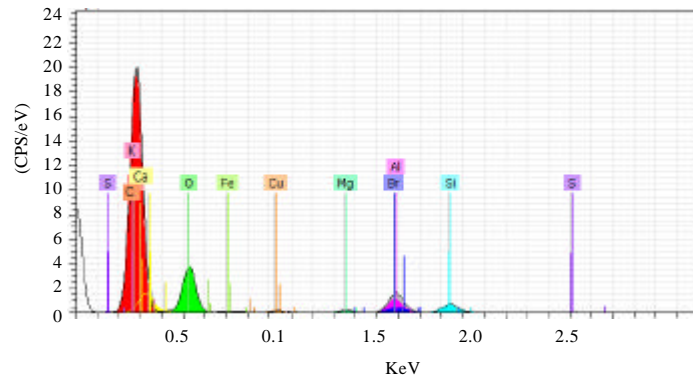
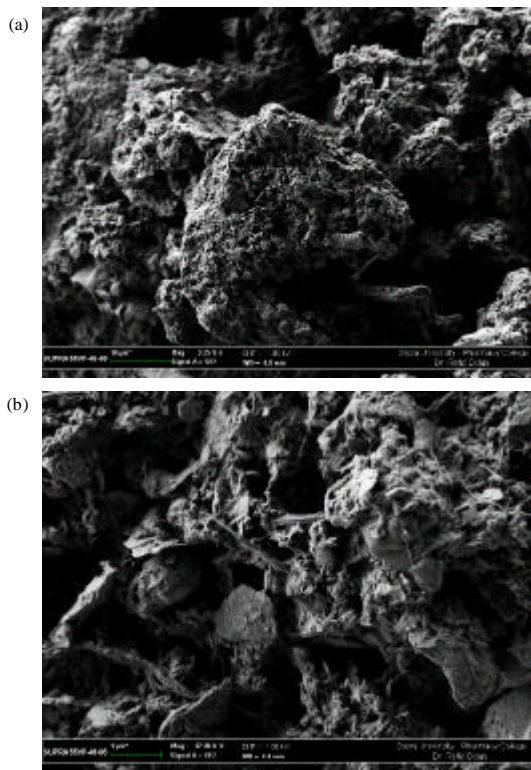Fig. 1: EDS analysis for GDAS

Fig. 2: SEM images of GDAS

(Goldstein *et al.*, 2013; Aljebore *et al.*, 2017). SEM was used for examining the surface texture of GDAS by ZEISS Supra 55vp, 2013, Germany. Figure 2 shows that the SEM of GDAS before sorption of BTEX, it is clear that the presence of holes and small openings on the surface also, a microporous network structure can be seen, thereby increasing the contact area which facilitates pore diffusion during the sorption/bio sorption process.

The tested chemicals was benzene from ROMIL-SA with purity 99.5%. The contaminant was dissolved in the distilled water to prepare the required concentration at room temperature.

Analysis: A High Performance Liquid Chromatography (HPLC) with UV-VIS detector was used to analysis the aqueous solution of benzene (ASTM D 6591-06, 2006). C18 (250*4.5 mm, BK0033) was used as stationary phase. The mobile phase is commonly a mixture of solvents that can be combined in certain ratios, acetonitrile/water with ratio 80/20 used as mobile phase that carried analytic with flow rate 1 mL/min and pressure of 14 MPa.

Sorption experiment: Batch experiments were conducted to obtain the equilibrium data and to specify the best conditions for treatment process. Several factors was investigated which affect the sorption efficiency such as sorbent dose contact time and initial contaminant concentration.

Validity of models: In the sorption equilibrium and kinetic isotherm studies, the optimization procedure requires an error function to be evaluated the fit of the isotherm to the experimental equilibrium data. The common error functions for determining the optimum isotherm parameters were the determination coefficient (R^2) and the Sum of Squared Errors (SSE) which are defined as (Ayawei *et al.*, 2017):

$$R^2 = \frac{\sum (q_{,cal.} - q_{m,\ exp.})^2}{\sum (q_{cal.} - q_{m,\ exp.})^2 + (q_{cal.} - q_{exp.})^2} \tag{1}$$

$$SSE = \sum_{i=1}^{n} \left(q_{cal.} - q_{exp} \right)^2 \tag{2}$$

Where:

q_{exp} = Amount of sorbate sorbed by sorbent during the experiment
q_{cal} = Amount of sorbate obtained by isotherm models
$q_{m,\ exp}$ = Average of q_{exp}
n = Number of data points

RESULTS AND DISCUSSION

Effect of adsorbent dose: The dependence of benzene sorption on GDAS dosage was studied by using
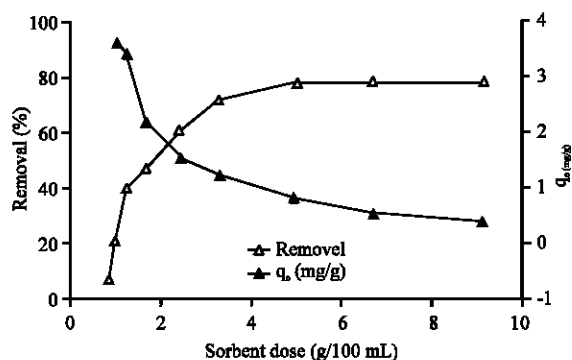
13

Fig. 3: Dependency of sorption on sorbent dose

Fig. 4: Dependency of sorption on contact time

Fig. 5: Dependency of sorption on of initial solute concentration

various amounts of granular dead biomass from 0.2-10 g are added to 100 mL of polluted solution for batch tests.

Figure 3 shows the benzene removal efficiency as a function of various quantities of sorbent dose. It is obvious that effectiveness improved with increasing GDAS from 0.2-10 g and then it fixed after a certain period of time. This was expecting because the greater dosage of sorbents in the solutions, the larger accessibility of sorption places. In addition, the results show that after a certain dosage of sorbent about 5 g/100 mL, the maximum sorption sets in and hence the amount of benzene bound to the sorbent and the amount of these contaminants in solution remains constant even with further addition of the sorbent dosage.

Figure 3 shows with increasing sorbent dose, the quantity sorbed per unit mass (q_e), reductions. The dwindling in sorption density with an excess in the sorbent dosage is mainly because of a sorption sites stay unsaturated during the sorption reactions whilst the number of site obtainable for sorption site growths by growing the sorbent dosage (Malik *et al.*, 2007; Yener *et al.*, 2006).

Dependency of sorption on contact time: An important aspect of the efficient and cost-effective implementation of the remediation treatment process is the equilibrium contact time. Shorter equilibrium contact time enhances the efficiency of the separation process (Kumar *et al.*, 2018).

Figure 4 show the effect of contact time on efficiency removal using optimal sorbent dose of GDAS (5 g/100 mL). This figure demonstrates that the percentage of removal of these pollutants increased significantly with increasing in interaction time. The sorption rate was fast at the first phase and progressively slowed down then. The slower sorption was probable because of the diminution in sorptions site on the surface of the GDAS.
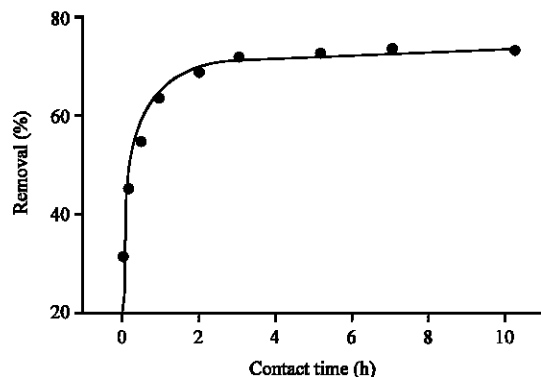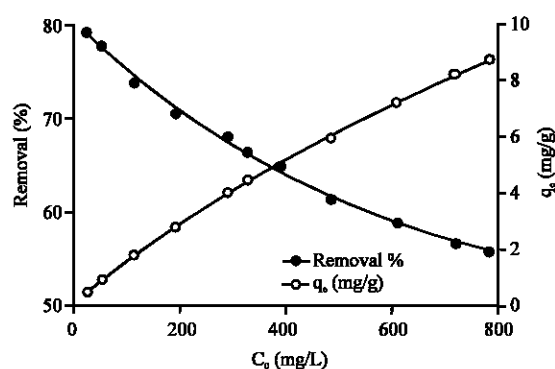
The kinetic data show that 75% of benzene was removed mainly within 5 h. There was no significant change in residual concentrations after these equilibrium times.

Dependency of initial concentration of contaminants on sorption efficiency: The effect of initial contaminate concentration on the sorption efficiency was examined under equilibrium conditions with GDAS dosage of 5 g/100 mL of benzene solution with concentration ranged from 25-700 mg/L. The results were shown in Fig. 5, it could be seen that by increasing the concentration of contaminant, the removal efficiency would decrease and the up take sorption q_e (mg/g) would increase. As a rule, increasing the initial concentration of contaminate results is an increase in the sorption capacity because it provides an important driving force to overcome all resistances of the benzene between the aqueous and solid phases, thus increasing the uptake.

In addition, increasing the initial benzene concentration increases the number of collisions between benzene and the sorbent which enhances the sorption process. However, the sorption effectiveness decrease, since, the sorbent has a restricted number of active sites

which saturates at a certain concentration. This denotes that the sorption capacity will growth with the increase of initial concentration mainly due to the increase in the mass transfer from the concentration gradient. Yet, the concentration will in reverse impact on the sorption efficiency because of the restricted sorption sites available for the uptake of contaminants (Husin *et al.*, 2011; Nourmoradi *et al.*, 2012; Gonte and Balasubramanian, 2016).

Equlibrai isotherm models: Sorption isotherms are smathematical models that describe the distribution of the sorbate species among liquid and sorbent, sorption data are described by Langmuir and Freundlich isotherm model. These isotherms relate metal uptake (q_e) per unit Mass (m) of sorbent to the equilibrium sorbate concentration in the bulk fluid phase (C_i):

$$q_e = \frac{V(C_0 - C_i)}{m} \quad (3)$$

where, V is the volume of solution in L.

The Langmuir isotherm: The Langmuir Model is based on the assumption that the maximum sorption occurs when a saturated monolayer of solute molecules is present on the sorbent surface. The Langmuir isotherm is given by Kumar and Kirthika (2009):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where, q_m and b are the Langmuir constants, representing the maximum sorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

It can be seen from Fig. 6, that the isotherm data have a good fitting to the Langmuir equation with ($R^2 = 0.998$) and SSE 0.123. The values of qm and b were determined from non-linear regression are listed in Table 2 were found to be 14.835 mg/g and 0.0033 L/mg, respectively.

The Freundlich isotherm: The Freundlich isotherm model is an empirical relationship describing the sorption of solutes from a liquid to a solid surface and assumes that different sites with several sorption energies are involved. Freundlich sorption isotherm is the relationship between the amounts of benzene sorbed per unit mass of GDAS, q_e and the concentration of the benzene at equilibrium, C_e (Vijayaraghavan and Yun, 2006):
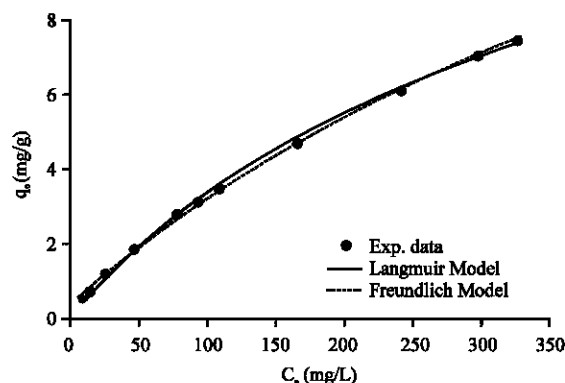
$$q_e = K_F C_e^{1/n} \quad (5)$$

Fig. 6: Sorption isotherm model for benzene removal onto GDAS

Table 2: Isotherm equilibrium data

Variables	Values
Langmuir Model	
q_m	14.8350
b	0.00333
R^2	0.99810
SSE	0.12290
Freundlich Model	
K_F	0.16340
n	1.48720
R^2	0.99820
SSE	0.11950

where, K_F and n are the Freundlich constants, the characteristics of the system. K_F and n are the indicators of the sorption capacity and sorption intensity, respectively. The ability of Freundlich model to fit the experimental data was shown in the Fig. 6 with determination coefficient (0.9982) and SSE (0.1195). The Freundlich constants K_F and n were found to be 0.163 and 1.487, respectively as seen from Table 2. The magnitudes of K_F and n show indicate favourable sorption of benzene by GDAS.

Kinetic Models: In order to investigate the controlling mechanism of sorption processes, the Pseudo-First-Order (PFM) and Pseudo-Second Order (PSM) equations are applied to model the kinetics of benzene sorption onto GDAS. The pseudo-first-order rate equation is given as (Ho, 2004; Lin and Wang , 2009):

$$q_t = q_e \left(1 - e^{-K_1 t}\right) \quad (6)$$

where, q_t and q_e (mg/g) are the quantities of sorbate removed from the aqueous solution at time t and at equilibrium, respectively and K_1 is the Pseudo first order rate constant (1/min).
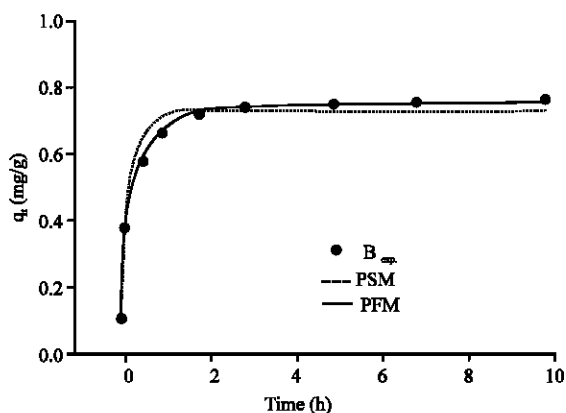
Fig. 7: Kinetic Models for sorption of benzene onto GDAS

Table 3: Constants of kinetic models

Variables	Values
Pseudo-first order	
$q_e^{EXP.}$ (mg/g)	0.7823
q_e (mg/g)	0.7177
K_1 (h^{-1})	4.2830
R^2	0.9563
SSE	0.0280
Pseudo-second order	
q_e (mg/g)	0.7583
K_2 (g/mg)	9.0820
R^2	0.9930
SSE	0.0037

Pseudo-second order model assumed that, the monolayer of sorbate is attached to the sorbent surface, energy of sorption is the same for each sorbent and there is no interaction between sorbed species. The kinetic form of this model is illustrated in the following expression (Bhattacharyya and Sharma, 2004):

$$q_t = \frac{K_2 q_e^2 t}{(1 + K_2 q_e t)} \qquad (7)$$

where, K_2 is the Pseudo second order rate constant (g/mg min).

Kinetic results data was well analyzed by the Pseudo first-order and Pseudo-second-order kinetic models (Fig. 7) and gave the best fitting for data depending on statistical error where (R^2) was >0.95 and the calculated sorption capacity q_e (mg/g) values were consistent very well with those obtained from experiments. The constants of these models were determined by using nonlinear regression method as listed in Table 3.

Mechanism of removal: Generally, the Intra-Particle Diffusion Model (IPD) is used to identify the mechanism of the sorption process. This model assumes that intra-particle diffusion is the rate-controlling step which
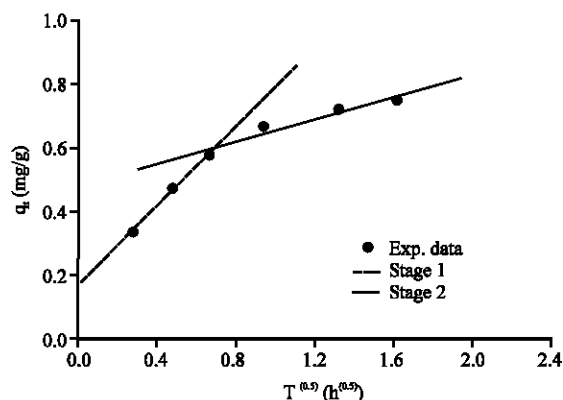

Fig. 8: IPD Model of benzene sorption from aqueous solution onto GDAS

Table 4: Constants of inta-particle diffusion model

Portions	Parameters	Values
1	k_{1B} (mg/g h$^{1/2}$)	0.4580
	I_{1B} (mg/g)	0.2155
	R^2	0.9921
	SSE	0.0152
2	k_{2B} (mg/g h$^{1/2}$)	0.1592
	I_{2B} (mg/g)	0.4669
	R^2	0.9298
	SSE	0.0241

is generally the case for well-mixed solutions. The intra-particle diffusion model is a single-resistance model in nature and might be described by Weber and Morris which is based on Fick's second law (Garcia *et al.*, 2014). The sorbed amount q_t should vary linearly with the square root of time. The intra-particle diffusion model can be described by the following equation (Kousha *et al.*, 2012):

$$q_t = k_{di} t^{\frac{1}{2}} + I_i \qquad (8)$$

where, k_{di} (mg/g h$^{1/2}$) is the rate constant of stage i and it is equal to the slope of relationship related q_t with $t^{1/2}$. Also, the intercept of stage i is represented by the value of I_i (mg/g) and it reflects the thickness of boundary layer. This means that the greater effect of the boundary layer can be recognized with the larger value of intercept. If the relationship correlated between q_t versus $t^{1/2}$ is linear, the intra-particle diffusion occurs. If the linear plot passes through the origin, the only intra-particle diffusion is represented the rate limiting process. Otherwise, other mechanisms must be considered with intra-particle diffusion (Yakout and Elsherif, 2010; Das, 2018). Intra-particle diffusion model was fitted the kinetic data. The results show in Fig. 8, two separate regions, the first severe portion attributed to the immediate sorption step and another portion is the intraparticle diffusion rate is dominated. The intra-particle diffusion coefficient for the sorption was listed in Table 4.

It is clear that the I_i for all stages are larger than zero and regression line didn't pass through the origin. This means the external mass transport mechanisms must be considered with intra-particle diffusion (Wu *et al.*, 2005). Also the results shown the constant rate k_{1B} for initial stage (surface sorption) is larger than of k_{2B} which obtain from second stage (internal diffusion), that's mean the sorption was governed by external sorption rather than intraparticle diffusion.

CONCLUSION

The GDAS sorption of benzene aqueous solution was investigated at different conditions. Results show the benzene removal efficiency as a function of various quantities of sorbent dose. It is obvious that effectiveness improved with increasing GDAS from 0.2-10 g and then it fixed after a certain period of time.

When increasing the sorbent dose the sorption density and the quantity sorbed per unit mass (q_e) are reduced.

The effect of contact time on efficiency removal shows that the percentage of removal of these pollutants increased significantly with growth in interaction time. The sorption rate was fast at the first phase and progressively slowed down then. Also, it could be seen that by increasing the initial concentration of contaminant the removal efficiency would decrease and the up take sorption would increase. The Langmuir and Freundlich isotherm model gave a good representation for sorption process with high determination coefficient.

The values of maximum up take (q_m) about 14.835 mg/g and Freundlich constants (K_F) and (n) were found to be 0.163 and 1.487, respectively which indicate favourable sorption of benzene onto GDAS.

Kinetic results data was analyzed by the Pseudo first-order and Pseudo-second-order kinetic models and gave the best fitting for data depending on statistical error where (R^2) was >0.95. The calculated sorption capacity q_e (mg/g) values agreed well with those obtained from experiments.

Intra-particle diffusion data was consisted from two separate regions; the first severe portion attributed to the immediate sorption step and another portion is the intraparticle diffusion rate is dominated. It is clear that the Ii for all stages is larger than zero and regression line didn't pass through the origin. This means the external mass transport mechanisms must be considered with intra-particle diffusion.

REFERENCES

ASTM D6591-06, 2006. Standard test method for determination of aromatic hydrocarbon types in middle distillates-high performance liquid chromatography method with refractive index detection. ASTM International, West Conshohocken, Pennsylvania, USA.

Aljeboree, A.M., A.N. Alshirifi and A.F. Alkaim, 2017. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. Arabian J. Chem., 10: S3381-S3393.

Ayawei, N., A.N. Ebelegi and D. Wankasi, 2017. Modelling and interpretation of adsorption isotherms. J. Chem., Vol. 2017. 10.1155/2017/3039817

Bhattacharyya, K.G. and A. Sharma, 2004. Adsorption of Pb (II) from aqueous solution by Azadirachta indica (Neem) leaf powder. J. Hazard. Mater., 113: 97-109.

Das, B., 2018. Equilibrium and kinetic studies on adsorption of copper from aqueous solution by Neem (Azadirachta Indica) bark powder. Intl. J. Sci. Res. Technol., 4: 290-298.

Garcia, E.R., R.L. Medina, M.M. Lozano, I.H. Perez and M.J. Valero *et al.*, 2014. Adsorption of AZO-dye orange II from aqueous solutions using a metal-organic framework material: Iron-benzenetricarboxylate. Mater., 7: 8037-8057.

Goldstein, J.I., D.E. Newbury, P. Echlin, D.C. Joy and C. Fiori *et al.*, 2013. Scanning electron microscopy and X-ray microanalysis: A text for biologists materials scientists and geologists. Plenum Press, New York, USA., ISBN-13:978-1-4613-3275-6, Pages: 673.

Gonte, R. and K. Balasubramanian, 2016. Heavy and toxic metal uptake by mesoporous hypercrosslinked SMA beads: Isotherms and kinetics. J. Saudi Chem. Soc., 20: S579-S590.

Ho, Y.S., 2004. Pseudo-isotherms using a second order kinetic expression constant. Adsorption, 10: 151-158.

Husin, N.I., N.A. Wahab, N. Isa and R. Boudville, 2011. Sorption equilibrium and kinetics of oil from aqueous solution using Banana pseudostem fibers. Proceedings of the 2011 International Conference on Environment and Industrial Innovation IPCBEE Vol. 12, February 26-28, 2011, IACSIT Press, Singapore, pp: 177-182.

IARC., 1989. IARC monographs on the evaluation of carcinogenic risks to humans. International Agency for Research on Cancer, Lyon, France.

Kousha, M., E. Daneshvar, M.S. Sohrabi, M. Jokar and A. Bhatnagar, 2012. Adsorption of acid orange II dye by raw and chemically modified brown macroalga Stoechospermum marginatum. Chem. Eng. J., 192: 67-76.

Kumar, N.S., M. Asif, M.I. Al-Hazzaa and A.A. Ibrahim, 2018. Biosorption of 2,4,6-trichlorophenol from aqueous medium using agro-waste: Pine (Pinus densiflora Sieb) bark powder. Acta Chim. Slovenica, 65: 221-230.

Kumar, P.S. and K. Kirthika, 2009. Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. J. Eng. Sci. Technol., 4: 351-363.

Lin, J. and L. Wang, 2009. Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of Methylene blue by activated carbon. Front. Environ. Sci. Eng. China, 3: 320-324.

Malik, R., D. Ramteke and S. Wate, 2007. Adsorption of malachite green on groundnut shell waste based activated carbon. Waste Manage., 27: 1129-1138.

Nourmoradi, H., M. Khiadani and M. Nikaeen, 2012. Multi-component adsorption of benzene, toluene, Ethylbenzene and Xylene from aqueous solutions by Montmorillonite modified with Tetradecyl Trimethyl Ammonium bromide. J. Chem., 2013: 1-10.

Simantiraki, F., C.G. Kollias, D. Maratos, J. Hahladakis and E. Gidarakos, 2013. Qualitative determination and application of sewage sludge and municipal solid waste compost for BTEX removal from groundwater. J. Environ. Chem. Eng., 1: 9-17.

Vijayaraghavan, K., T.V.N. Padmesh, K. Palanivelu and M. Velan, 2006. Biosorption of nickel (II) ions onto Sargassum wightii: Application of two-parameter and three parameter isotherm models. J. Hazard. Mater., 133: 304-308.

Wu, Z., H. Joo and K. Lee, 2005. Kinetics and thermodynamics of the organic dye adsorption on the mesoporous hybrid xerogel. Chem. Eng. J., 112: 227-236.

Yakout, S.M. and E. Elsherif, 2010. Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons. Carbon Sci. Technol., 3: 144-153.

Yener, J., T. Kopac, G. Dogu and T. Dogu, 2006. Adsorption of basic yellow 28 from aqueous solutions with Clinoptilolite and amberlite. J. Colloid Interface Sci., 294: 255-264.

Youngren, S.H., E.A. McKenna, T.B. Piccin, J.R. Schroeder and S.R. Baker, 1994. Evaluation of the total petroleum hydrocarbon standard at jet fuel contaminated air force sites. EA Engineering, Science and Technology, Inc., Hunt Valley, Maryland, USA.