Removal of 2,4-Dinitrophenol by adsorption onto activated carbon prepared from date stones, Kinetic and isotherm studies.

Bahdja HAYOUN [1], Nabila BENKHELAT[2], Mustapha BOUROUINA[1], Saliha BOUROUINA-BACHA[3]

1:Department of Chemistry, Faculty of Exact Sciences, University of Bejaia, Bejaia 06000, Algeria,email:hayba.bahdja@gmail.com, bouryas@yahoo.fr

2: Department of Environmental Biological Sciences, Faculty of Natural and Life Science, University of Bejaia, Bejaia 06000, Algeria, email: toutaben1011@gmail.com

3: Department of Process Engineering, Faculty of Technology, University of Bejaia, Bejaia 06000, Algeria, email:lgebej@yahoo.fr

Date of submission: 01/06/2020 Date of acceptance: 09/02/2021 Date of publication: 16/03/2021

Abstract

The present study deals with the preparation, characterization of an activated carbon (AC) based a lignocellulosic material, date stones (DS) by chemical process using the zinc chloride ($ZnCl_2$) as activating agent that produce a large development of porosity, and its application for adsorption of 2,4-Dinitrophenol (2,4-DNP) from aqueous solution.

The surface characteristics of the activated carbon prepared were also studied using the Scanning Electron Microscopy (SEM) and liquid displacement method. Batch studies were performed to evaluate the influence of contact time, initial 2,4-DNP concentration and AC dosage. The experimental data were analysed using Langmuir, Freundlich and Temkin isotherm models. The results of the study indicated that the AC adsorption data are best described by the Langmuir isotherm (correlation coefficient R^2= 0.998, Average relative error ARE<4.0), and the maximum adsorption capacity was found to be 196.078 mg g^{-1} at room temperature (25±2°C). The pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to modeling the adsorption kinetics. Adsorption reaction data are best fitted by the pseudo-second order kinetics (R^2> 0.995, ARE<6.0) for all range 2,4-DNP concentrations. Overall, date stones (DS) offered low-cost adsorbent for the preparation of activated carbon with a high removal capacity for 2,4-DNP from water in less than 2hours.

Keywords: *Adsorption, activated carbon, date stones, 2,4-Dinitrophenol,isotherm, kinetic*

I. Introduction

Nowadays, due to vast sources of pollution, hazardous compounds removal has become one of the crucial issues among industrial companies and nations, this is because of their human toxicity and environment [1,2]. Phenolic compounds are amongst the most common organic pollutants found in many industrial wastewaters [3-5]. Among the latter, the 2,4-Dinitrophenol (2,4-DNP), is widely applied as antioxidants, flavoring agents and in to production of organic synthesis. Hence, a large quantity of wastewater containing 2,4-DNP occurs [3,6]. Moreover, mutagenic and carcinogenic toxicity effects toward humans and other living organisms have been directly attributed to 2, 4-DNP due to their volatility and high solubility in water[6-8].

Therefore, several physical, chemical and biological treatment methods are used to remove the 2,4-DNP from wastewater [6,8]. Among these, the adsorption method is more useful and feasible method owing to its excellent properties such as, easy-to-use, low cost, high efficiency, etc [9,10]. Meantime, a large number of adsorbents have been sprung up, among them, activated carbon has been found to be superior because of its in adsorbing efficiently a wide range of different types of adsorbates [1,11]. However, commercially available activated carbons are still considered expensive [1,12]. This has led to the study of relatively inexpensive and abundant materials which can serve as cheap adsorbents and at the same time endowed with reasonable adsorption capacity [12, 13].

In recent years, there are many studies on the production of activated carbons from agricultural by-products and waste [9, 11, 13]. Furthermore, there are two different processes for the preparation of activated carbons: physical activation and chemical activation [11]. However, let us compare the two methods; there are two important advantages of chemical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn-off char is not required [3,11, 14].

Hence, the aim of this study is to value an agricultural waste, the date stones, as abundant and cheap precursor for activated carbon production by chemical process and to study its removal efficiency of 2,4-Dinitrophenol. The influence of adsorbent-adsorbate contact time, 2,4-DNP initial concentration and adsorbent dosage were evaluated. The equilibrium data obtained in a batch reactor were fitted by isotherm models of Langmuir, Freundlich and Temkin. The kinetic data were evaluated by pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models.

II. Materials and methods

2.1 Materials

Date stones (DS) were used as raw material for the preparation of AC. They were chosen in this study because of their abundance and availability compared to other biomass.2,4-Dinitrophenol (designated as 2,4-DNP) was selected as a organic contaminant, with chemical properties of: purity > 98%, pKa 4.9, molecular weight 184.11 g mol^{-1}, Solubility in water 2.97 gL^{-1}, CAS n° : 51-28-5 from Merck (BIOCHIM Chemopharma). The Zinc Chloride ($ZnCl_2$) of purity > 98%, Molecular weight 136.3 g mol^{-1}, CAS n° : 7646-85 and BIOCHIM CHEMOPHARMA brand was used for the treatment of date stones. Diluted solutions (0.1 M) of HCl (hydrochloric acid, purity 37%, density 1.18, molecular weight 36.5g mol^{-1} and SIGMA-ALDRICH brand) and NaOH (soda, purity 97%, molecular weight 40 g mol^{-1} and BIOCHEM CHEMOPHARMA brand) were used to adjust the pH of solutions. All solutions were prepared with distilled water of a conductivity of 1-2 µs.

2.2 Preparation of activated carbon

First of all, the DS have been previously repeatedly washed with distilled water (hot then cold washing) to remove inorganic impurities, filtered and dried in oven for 24 h at 105°C to reduce the moisture content. Finally, the dried biomass was ground and sieved to get a particle size $\leq$ 0.5 mm.

A two-step procedure was applied for the preparation of activated carbon from DS, impregnation with zinc chloride ($ZnCl_2$) as activating agent and carbonization. 15 g of $ZnCl_2$ were dissolved in 150 mL of distilled water, and then 10 g of dried DS (fraction $\leq$0.5 mm) was mixed with the zinc chloride solution and maintained heating under reflux at 85 °C for 2 h. The mixture was dehydrated in an oven at 105 °C for about 24 h. The $ZnCl_2$ impregnated fraction was placed in a ceramic crucible and pyrolyzed in a furnace under the nitrogen flow . The sample was heated to final temperature of 550°C with 10 °Cmin^{-1} heating rate for residence time of 2 h. The resultant activated carbon was washed with 3 M HCl solution by heating under reflux at around 90 °C for 30 min, filtered and rinsed by warm distilled water until neutral pH, dried at 105 °C in an oven for about 12 h. Finally, the activated carbon (designated AC) was then stored in desiccator for characterization and later use in adsorption experiments.

2.3 Characterization of activated carbon

The morphologies of the AC were analyzed using a Scanning Electron Microscope (SEM) FEI Quanta FEG 250 from the University of Lyon 1, France. The apparent density (bulk density), real density, porous volume and porosity of the AC were measured by the liquid displacement method[15]. The apparent density (bulk density) ρapp (g cm^{-3}) was calculated by filling a calibrated cylinder with a given adsorbent weight (m_{ads}) and tapping the cylinder until a minimum volume is recorded. This latter represents the apparent volume (V_{app}) of AC; thus, the apparent density of AC was evaluated using the following equation:

$$\rho_{app} = \frac{m_{ads}}{V_{app}} \qquad (1)$$

However, the real density$\rho real$ (gcm^{-3}) was established by filling a pycnometer with a definite mass of the adsorbent (m_{ads}).

Then, the pycnometer thus filled was adjusted to its volume (V_{pyc}) by adding volume of a displacement liquid which is methanol (99% purity) (V_{meth}, m_{meth}) and was weighed (m_{T}). The real density was calculated using the following equations :

$$\rho_{real} = \frac{m_{ads}}{V_{real\,of\,adsorbent}} \qquad (2)$$

Subsequently, knowing the density of our adsorbent (AC), its porous volume $P.V$(cm^{3}g^{-1}) and its porosity $\mathcal{E}$ of AC were easily calculated using the following equations:

$$P.V = \frac{1}{\rho_{app}} - \frac{1}{\rho_{real}} \qquad (3)$$

$$\mathcal{E} = 1 - \frac{\rho_{app}}{\rho_{real}} \qquad (4)$$

2.4 Adsorption experiments

The adsorption experiments were performed in an Erlenmeyer flask (500 mL) that contained 250 mL of 2,4-DNP solution on an magnetic stirrer at a speed of 300 rpm and at room temperature (25±1 °C). A parametric study was carried out where the effect of contact time and initial 2,4-DNP concentration 65 -170 mg L^{-1}on adsorption capacity of AC were examined. However, the pH of solution was kept fixed, pH=6.

To that end, the samples were withdrawn from the Erlenmeyer at predetermined time intervals. The 2,4-DNP solution is separated from the AC using a Hettich brand centrifuge at 5000 rpm for 5 minutes and analyzed for their 2,4-DNP content spectrophotometrically at the wavelength $\lambda_{\max}$ = 354 nm using a UV spectrophotometer (Shimadzu). The pH of 2,4-DNP solution has been adjusted using HCl and NaOH solutions (0.1 M). All experiments were performed in duplicate, all data being calculated and average values taken to represent the results.

The 2,4-DNP removal efficiency R(%) was calculated as follows:

$$R\,\% = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (5)$$

The amount of 2,4-DNP adsorbed onto AC was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (6)$$

Where q_t is the amount of 2,4-DNP adsorbed on the AC (mgg^{-1}), C_0 and C_t are the liquid phase concentrations of 2,4-DNP at initial and equilibrium, respectively. V (L) is the volume of 2,4-DNP solution and m (g) is the dose of the AC used. The average relative error is calculated from this equation [16]:

$$ARE = \sum_{i=1}^{N} \left| \frac{q_{e,exp} - q_{e,model}}{q_{e,exp}} \right|_i \quad (7)$$

Where :q_{eexp} and q_{emodel} (mg g^{-1}) are the uptake at equilibrium measured (exp) and calculated (model) by the isotherm model, respectively. We also used the same relationship to determine the mean relative errors for the kinetic models.

2.5 Data analysis

Table 1. **P**hysical characteristics of AC.

Parameters	Values
Porosity (%)	91.4
Porous volume (cm^3g^{-1})	2.479
Apparent density (gcm^{-3})	0.328
Real density (gcm^{-3})	3.832

III. Results and discussion

3.1 Characterization

A. Morphology of AC

The morphology of AC examined by SEM, is illustrated in Fig.1. The SEM micrograph clearly shows that the AC has an featured irregular and porous surface, which allows the 2,4-DNP molecules to penetrate into the pores and attach to host sites.

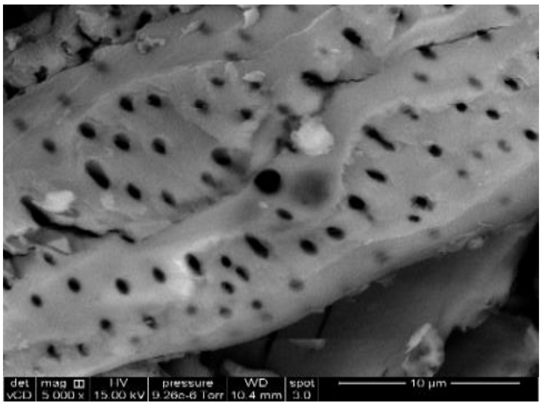

Figure 1. SEM micrograph of AC.

B. physical characteristics of AC

Table 2. General forms of the isotherm and kinetic models used in this study.

	form	Equation no.	Reference
Isotherm models			
Langmuir	$q_e = \frac{q_m . K_L . C_e}{1 + K_L . C_e}$	(8)	[17]
Freundlich	$q_e = K_F . C_e^{1/nf}$	(9)	[18]
Temkin	$q_e = B_T . ln\ (K_T . C_e)$	(10)	[19]
Kinetic models			
Pseudo-first-order (PFO)	$q_t = q_e(1 - e^{-k_1 t})$	(11)	[20]
Pseudo-second-order (PSO)	$q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t}$	(12)	[21]
intra-particle diffusion (IPD)	$q_t = K_3\sqrt{t} + c$	(13)	[22]

3.2 Effect of adsorbent-adsorbate contact time and initial 2,4-DNP concentration

The effect of contact time (0-180 min) and various initial 2,4-DNP concentrations (65–180 mg L^{-1}) on removal efficiency of 2,4-DNP onto AC at a fixed AC dosage 0.5 g L^{-1} and pH 6 at room temperature were studied. The results are shown in Fig. 2. According to these latter, the removal efficiency of 2,4-DNP increased dramatically in the initial stages, whereas, with increase of contact time the removal efficiency gradually gets increased and reaches equilibrium at about 120 min with a maximum value of 87.89 % for an initial concentration of 65 mg L^{-1}. The removal efficiency was drastic in the initial contact time due to availability of the reactive site on the surface of the AC [2,10]. Moreover, no significant changes were observed in the removal efficiency after equilibrium due to the slow pore diffusion or saturation of AC [5,15]. We can also clearly see that an increase in the initial 2,4-DNP concentration from 65mg L^{-1} up to 170 mg L^{-1} decreases the removal efficiency from 87.89% to 54.38 % which can be explained by considering that at a lower initial 2,4-DNP concentration, the ratio of the adsorbent active sites to the total adsorbate is high and therefore all adsorbate molecules can interact with adsorbent (AC) and be removed from the solution [1].

The study of the effect of contact time and initial 2,4-DNP concentration allowed us to set an optimum equilibrium time of 120 min and concentration of 65 mg L^{-1} for the rest of the study.

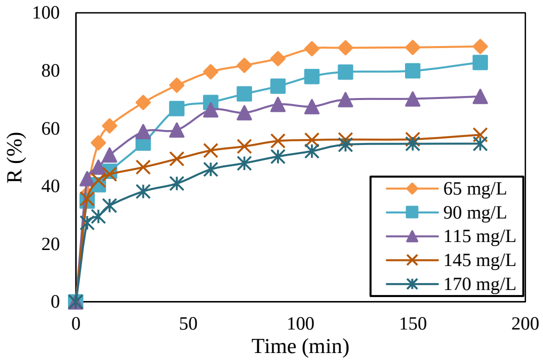

Figure 2. Evolution of removal efficiency of 2,4-DNP in terms of contact time and initial 2,4-DNP concentration at : AC dose: 0.5 g L^{-1}, pH 6.0, flask shaking at 300 rpm at 25 °C

3.3 Effect of adsorbent dosage

The adsorbent dosage of adsorption process in terms of the economic aspects is very important parameter for wastewater treatment applications. A adsorbent dosage optimization for the above system was therefore carried out with five different AC dosages ranging from 0.1 to 1 g L^{-1}with 2, 4-DNP concentration 65 mg L^{-1}, contact time 120 min, initial pH 6 at room temperature (25°C) .The experimental results are given in Fig. 3. The removal efficiency of 2,4-DNP increased from 65.21 to 97.36 % with increase of adsorbent dose from 0.1 to 1 g L^{-1}. This increase in adsorption of 2,4-DNP with increase of AC dose is very common and is reported in literature [7]. It can therefore be attributed to the increase in the number of active sites of the adsorbent, which led to easier penetration of the 2,4-DNP into the sorption sites[7], as well as the porous nature of AC surface as shown in SEM image (Fig. 1).

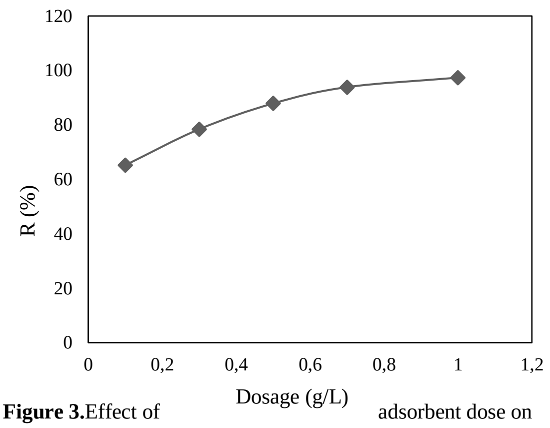

Figure 3. Effect of adsorbent dose on the removal efficiency of 2,4-DNP onto AC at : initial 2,4-DNP concentration 65 mg L^{-1}, pH 6, flask shaking at 300 rpm at 25 °C

3.4 Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. In general, the adsorption isotherm describes how adsorbates interact with adsorbents and this is critical in optimizing the use of adsorbents [12, 16, 23]. In this study, the isotherm models of Langmuir, Freundlich, and Temkin were fitted to the experimental data of 2,4-DNP adsorption onto AC. The results for the linear adjustments of the isotherm models to the experimental equilibrium data are presented in Table 3.

Table 3. Parameters of the adsorption isotherm models.

Isotherms models	Parameters	Values	*R*^{2}	*ARE (%)*
Langmuir	q_m (mg g^{-1}) K_L (L mg^{-1}) R_L	196.078 0.129 0.221- 0.378	0.988	3.92
Freundlich	K_F(mg1$^{-(n-1)}$ l^{n-1} g^{-1}) n_F	76.172 5.03	0.809	7.67
Temkin	K_T (L g) B_T (kJ mol^{-1})	1.754 29.412	0.835	4.29

According the Langmuir model, the Langmuir separation factor (R_L) indicates if the adsorption process is irreversible (R_L = 0), favorable (0 <R_L> 1), linear (R_L = 1) or unfavorable (R_L> 1). For the value range of concentrations studied (65-170 mgL^{-1}), the R$_L$ values were 0.221 – 0.378 that confirming the favorability of 2,4-DNP adsorption onto AC with maximum adsorption capacity q_m = 196.078 mg g^{-1}[17,23].

Further, according to the Freundlich model, the exponent n_F determines the adsorption effectiveness. According to the results, the values of n_F were higher than 1, suggesting that 2,4-DNP was favorably adsorbed by the AC in the concentration range studied [18,23].

The Temkin constant, B_T, is related to the heat of adsorption, which indicates if the adsorption reaction is endothermic (B_T< 1J mol^{-1}) or exothermic (B_T> 1 $Jmol^{-1}$). The B_T values were 29.412 $Jmol^{-1}$, that indicating the exothermic nature of 2,4-DNP adsorption onto AC [19,23].

In closing, the Langmuir adsorption isotherm model yielded the best fit as indicated by the highest correlation coefficient (R^2> 0.988), as well as a lower mean relative error (ARE = 3.92%) compared to the Freundlich and Temkin isotherm models [5,10].

3.5 Adsorption kinetics

Adsorption kinetic describes the mechanism of adsorption processes which in turn controls the equilibrium time and mass transfer of the adsorbate. The experimental data of 2,4-DNP adsorption at different time intervals were examined with pseudo-first-order(PFO), pseudo second-order (PSO) and intra-particle diffusion (IPD) models [9, 10]. The constants obtained from these three kinetic models are given in Table 4. The results show us that the correlation coefficient, R^2 values for the second-order kinetic model were the highest all 2,4-DNP concentrations (R^2 = 0.995-0.999). Moreover, the experimental q_e values agreed satisfactorily with the calculated q_e values, for 2,4-DNP initial concentration ranging from 65 to 170 mg L^{-1}, which suggested that the adsorption system follows pseudo-second-order model [5,7,10].

Hence the intra-particle model of weber and Morris (IPD) was used to clarify the adsorption mechanism. According to this latter, a plot of q_t versus $\sqrt{t}$ should be linear if intra-particle diffusion is involved in the adsorption process, and if this line passes through the origin the intra-particle diffusion is the rate controlling step. As can be seen from Fig. 4, the linear plots at each concentration did not pass through the origin, which indicates that the intra-particle diffusion was not only a rate controlling step [13].

Table 4. Kinetic parameters of the adsorption of 2,4-DNP on the AC following different kinetic models.

[2,4-DNP]o (mg L^{-1})	**65**	**90**	**115**	**145**	**170**
q_e(exp) (mg g^{-1})	114.86	146.67	156.94	163.06	185.09
Pseudo-first order model (PPO)					
q_1(mg g^{-1})	83.88	102.51	64.12	88.89	103.16
k_1(min^{-1})	0.039	0.029	0.027	0.043	0.022
R^2	0.854	0.962	0.925	0.918	0.963
ARE (%)	11.705	11.744	11.683	11.667	11.742
Pseudo-second order model (PSO)					
q_2(mg g^{-1})	121.95	161.29	163.93	172.41	200
k_2(g mg^{-1} min^{-1})	$0.94.10^{-3}$	$0.45.10^{-3}$	$0.9. 10^{-3}$	$0.96. 10^{-3}$	$0.39. 10^{-3}$
R^2	0.999	0.997	0.999	0.999	0.995
ARE (%)	4.397	5.011	6.752	5.476	6.179
Intra-particle diffusion model (IPD)					
K_{IPD1} (mg g^{-1} $min^{0,5}$)	7.099	10.141	7.282	6.876	10.638
C_{IPD1}(mg g^{-1})	46.115	44.91	84.517	97.01	70.051
R^2	0.917	0.975	0.941	0.957	0.996
K_{IPD2} (mg g^{-1} $min^{0,5}$)	0.287	2.543	2.099	1.509	0.481
C_{IPD2}(mg g^{-1})	111.61	117.86	131.75	146.53	179.84
R^2	0.957	0.901	0.763	0.756	0.882

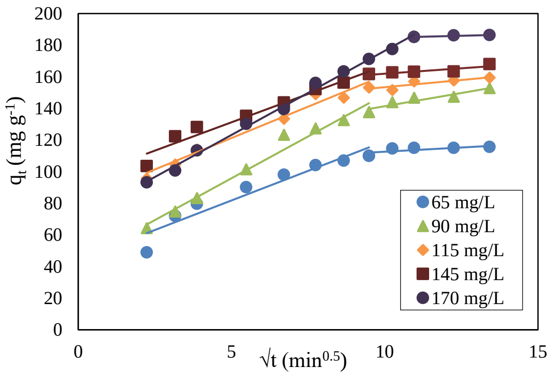

Figure 4. Linear kinetic plots intra-particle diffusion model of adsorption of 2,4-DNP onto AC

V. Conclusion

The present study shows that the activated carbon synthesized from date stones is an effective adsorbent for the removal of 2,4-DNP from aqueous solution. A higher percentage (97.36 %) of 2,4-DNP removal has been obtained at pH 6, applying a dose of 1 gL^{-1} of AC and for an equilibrium time of 120 min at room temperature (25±2°C).

The isotherm and kinetic models analyses revealed that the experimental data well fitted to the pseudo-second-order model and Langmuir isotherm, respectively with maximum adsorption capacity q_m = 196.078 mg g^{-1}. It was found that the intra-particle diffusion was not only a rate controlling step; hence, the adsorption process was found to be controlled by external mass transfer at the earlier stages and by intra-particle diffusion at the later stages. As an overall conclusion, the date stones may be classified as cheap precursor for activated carbon production that showed excellent adsorptive characteristics for removal 2,4-DNP from aqueous solution.

List of symbols

DS: date stones
AC: activated carbon
2,4-DNP: 2,4-Dinitrophenol
SEM: Scanning Electron Microscopy
ρapp: apparent density (g cm^{-3})
ρreal real density(gcm^{-3})
P.V : porous volume (cm^{3}g^{-1})
Ɛ: porosity (%)
m: mass of adsorbent (g)
T: Temperature (C°)
V: Volume (L)
C_0: Initial concentration (mg L^{-1})
C_e: equilibrium concentration (mgL^{-1})
C_t: concentration at time t (mgg^{-1})
q_e: equilibrium uptake (mgg^{-1})
q_m: maximum uptake (mgg^{-1})
q_t; uptake at time t (mgg^{-1})
R: removal efficiency (%)
K_L: Langmuir constant (L mg^{-1})
K_F: Freundlich constant (mg1$^{-(n-1)}$ l^{n-1} g^{-1})
K_T: Temkin constant (Lg^{-1})
n_F: Freundlich coefficient
R_L: Separation factor of Langmuir model
B_T : Temkin constant related to the heat of adsorption (kJmol^{-1})
k_1:pseudo-first-order constant(min^{-1})
k_2: pseudo second-order constant (g mg^{-1} min^{-1})
k_{IPD} : intra-particle diffusion rate constant (mg g^{-1} min^{0,5})
C_{IPD} :intra-particle diffusion constant(mg g^{-1})
R^2: correlation coefficient
ARE:average relative error (%)

References

1. A. B. Leite, C. Saucier, E. C. Lima, G. S. dos Reis, C. S. Umpierres, B. L. Mello, M. Shirmardi, S. L.P Dias and C. H. Sampaio: Activated carbons from avocado seed: optimisation and application for removal of several emerging organic compounds,Environ Sci Pollut Res, 25 (2018) 7647-7661.

2. S. Yari, S. Abbasizadehb, S.E. Mousavib, M.S. Moghaddamc and A.Z. Moghaddam: Adsorption of Pb(II) and Cu(II) ions from aqueous solution by an electrospun CeO_2 nanofiber adsorbent functionalized with mercapto groups,Process Saf Environ Prot, 94 (2015) 159-171.

3. A. Dąbrowski, P. Podkościelny, Z. Hubicki and M. Barczak: Adsorption of phenolic compounds by activated carbon-a critical review,Chemosphere, 58 (2005) 1049-1070.

4. B. Das, T.K. Mandal and S. Patra: A comprehensive study on Chlorella pyrenoidosa for phenol degradation and its potential applicability as biodiesel feedstock and animal feed,Appl Biochem Biotech, 176 (2015) 1382- 4010.

5. Y. Pan, Z. Li, Z. Zhang, X.S. Tong, H. Li, C.Z. Jia, B . Liu, C.Y. Sun, L.Y. Yang and G.J. Chen:

6. Adsorptive removal of phenol from aqueous solution with zeolitic imidazolate framework-67, J Environ Manage, 169 (2016) 167-173.

7. Z.L. She, M.C. Gao, C.J. Jin, Y.Y. Chen and J.W. Yu: Toxicity and biodegradation of 2,4-dinitrophenol and 3-nitrophenol in anaerobic systems,Process Biochem, 40 (2005) 3017-3024.

8. T.H. Pham, B.K. Lee, J.T. Kim and C.H. Lee: Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite, Mater Design, 101 (2016) 210-217.

9. T. Tang, Zh Yue, J. Wang, T. Chen and Ch. Qing: Goethite promoted biodegradation of 2,4-dinitrophenol under nitrate reduction condition,J. Hazard. Mater., 343 (2018)176-180.

10. W. Zhang, H. Li, X. Kan, L. Dong, H. Yan, Z. Jiang, H. Yanga, A. Lia and R. Cheng: Adsorption of anionic dyes from aqueous solutions using chemically modified straw, Bioresour. Technol., 117(2012) 40-47.

11. R. Kumar and M.A. Barakat: Decolourization of hazardous brilliant green from aqueous solution using binary oxidized cactus fruit peel, Chem Eng J, 226 (2013) 377-383.

12. V.S. Tran, H.H. Ngo, W. Guo, J. Zhang, S. Lian g, C. Ton-That and X. Zhang: Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water, Bioresour. Technol., 182 (2015) 353-363.

13. M. Bergaoui, A. Nakhli , Y. Benguerba , M. Khalfaoui , A. Erto , F.E. Soetaredjo , S. Ismadji and B. Ernst: Novel insights into the adsorption mechanism of methylene blue onto organo-bentonite: Adsorption isotherms modeling and molecular simulation, J. Mol. Liq., 272 (2018) 697-707.

14. Zh.Hao, C.H. Wang, Z.Sh yan, H.L. Jiang and H.Ch Xu: Magnetic particles modification of coconut shell-derived activated carbon and biochar for effective removal of phenol from water, Chemosphere, 211 (2018) 962-969.

15. N.Z. Al-Mutairi: 2,4-Dinitrophenol adsorption by date seeds: Effect of physico-chemical environment and regeneration study, Desalination, 250 (2010) 892-901.

16. M.K. Narbat, F. Orang, M.S. Hashtjin and A. Goudarzi: Fabrication of porous hydroxyapatite-gelatin composites caffolds for bone tissue, engine, Iranian biomedical journal, 10 (2006) 215-223.

17. M.M. Seyed, N.K. Soheil, P. Mohammad, A. Nima, V. Leila and M. Gordon: Methylene blue adsorption via maize silk powder: Kinetic, equilibrium, thermodynamic studies and residual error analysis, Process Saf Environ Prot, 6 (2017) 191-202.

18. I. Langmuir: The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc., 38 (1916) 2221–2295.
19. H.M.F. Freundlich: Über die adsorption in lösungen, Z. Phys. Chem., 57 (1906) 385–470.

20. M.J. Temkin, V. Phyzev: Recent modifications to Langmuir isotherms, Acta Physiochim, USSR, 12 (1940) 217–222.

21. S. Langergen and B.K. Svenska: Zur theorie der sogenannten adsoption geloester stoffe,Veteruskapsakad Handlingar, 24 (1898) 1–39.

22. Y.S. Ho and G. Mckay: Pseudo-second order model for sorption processes, Process Biochem, 34 (1999) 451–465.

23. W.J. Weber and J.C. Morris: Kinetics of adsorption on carbon from solution, J. Saint. Eng. Div. Am. Soc. Civil Eng. ,89 (1963) 31–60.

24. K.Y. Foo and B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem Eng J, 156 (2010) 2–10.