Egypt. J. Chem. **Vol. 65**, No. 5 pp. 85 - 92 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Removal of Heavy Metals Using Ecofriendly Adsorbents Prepared from Modified Agricultural Wastes

Hala E.Ghannam

Pollution Laboratory, Freshwater and lake division, National Institute of Oceanography and Fisheries (NIOF), Egypt.

Abstract

In recent years a great attention has been focused on preparing highly efficient, cheaper and ecofriendly adsorbents which used for heavy metals removal from wastewater. This work deals with the use of sugarcane bagasse (SCB) adsorbent for removal of Fe (III), Mn (II) and Pb (II). SEM and FTIR spectroscopy were used for characterization of the prepared adsorbent. Also the adsorption effects under different conditions of pH, adsorbent weight, initial metal concentrations, contact time and temperature on the percent of heavy metals removal were investigated. Adsorption isotherm investigation indicated that, Fe metal was fitted to Temkin model, where Mn and Pb metals were fitted to the Freundlich model. The study of thermodynamic parameters showed that, the negative values of ΔG° indicated that the adsorption of (Fe, Mn and Pb) on SCB is a spontaneous process.

Keywords: heavy metals; sugarcane bagasse; Adsorption isotherm

Introduction

Pollution with heavy metals is serious threats to the environment; these metals inter to aquatic system through several industrial activities like, mining, fertilizer industries, paper industries, and pesticides [1]. Pollution affects ecosystems and human health, aquatic plants and animals. Heavy metals like chromium, iron, cadmium, lead, copper, and zinc classed as dangerous materials to all life forms [2]. The recovery of heavy metals from polluted water has a greet attention not only to remove their poisons effect, but also to treat precious materials. There are several treatment methods to remove these metals from polluted water [3] but, these ways have a lot of mistakes such as less efficiency and sensitive system conditions [4]. The adsorption of heavy metals by low cost agricultural waste materials has attracted much attention [5-6]. Biosorption used materials from agricultural wastes have many benefits like its great efficiency in adsorption, not expensive, lower biological or chemical wastes and possibility of regeneration [7-8]. The use of sugarcane bagasse (SCB) as an ecofriendly material in heavy metals removal is important due to many properties like easy method for preparation, not expensive and the useful reuse of agricultural wastes [9 - 10]. SCB can defined also as cellulosic materials, as a result of their structures that include (25% hemicellulose, 50% cellulose, and 25% lignin) [11]. The maximum efficiency in adsorption of SCB is related to the presence of different functional groups like acetamido, alcoholic, amino, amido, and sulfhydryl [12]. The rate at which adsorption happen has a great attention because of its importance in the adsorption process. The effect of several parameters on the adsorption rate has been investigated to estimate the best operating conditions. Specifically, contact time, solution pH, temperature, adsorbent weight and concentration have been known as parameters that affect the adsorption rate [2]. In adsorption system there are several kinetic models used for describing the dynamic process among them both Langmuir and Freundlich are used to give the relation between the adsorbed weight of solid sorbent, and the amount of solute non-adsorbed at equilibrium [13]. For adsorption of heavy metal on sorbent materials these kinetic models show great results for the relation between the adsorbed material and metal at equilibrium concentration of solute at and constant temperature [14]. In this work the aims were classified into three steps:

*Corresponding author e-mail: drhalaghannam@yahoo.com; (**Hala E.Ghannam**)
Receive Date: 15 July 2021, Revise Date: 20 October 2021, Accept Date: 27 October 2021
DOI: 10.21608/ejchem.2021.86542.4183

1. Preparation of bio-sorbent from the agricultural waste and characterization using SEM and FTIR spectroscopy.
2. The prepared sorbent was examined for the removal of (Fe, Mn and Pb) under different adsorption condition.
3. The isotherm models and thermodynamic parameters were investigated to examine of the adsorption behavior.

Materials and Methods

Preparation of sugarcane bagasse

Sugarcane bagasse (SCB) was firstly washed thoroughly with distilled water to remove the dust particles, then soaked overnight in 0.1N NaOH solution and again washed well with double distilled water. SCB was then soaked in 0.1 N CH_3COOH for 2-3 h to remove the traces of NaOH. It was thoroughly washed again with double distilled water till the wash water became colorless and then filtered, well dried, powdered and sieved before use [15].

Characterization of the adsorbent

Scanning electron microscopy (SEM) having a magnification range of 5,000 and accelerating voltage 20 kV were used for characterization of prepared SCB.

FTIR spectroscopy

The Fourier transform infrared (FT-IR) spectra were monitored via a single beam thermo scientific Nicolet iS10 instrument. The samples were grounded with KBr (1:100) to form tablets, and thus confined into the sample holder in the spectrometer cavity to record the measurements in the 4000-400 cm^{-1} region.

Adsorbates

All the chemicals used in the study were of analytical grade and obtained from Sigma-Aldrich. Stock solutions of 1000 mg/l strength of Fe(II), Mn(II) and Pb(II) metal ions were prepared and diluted to give metal ion concentration in the range of 50-200 mg/l for use in the experiments.

Adsorption experiments

For each experimental run, 100 ml aqueous solution of a known concentration of one of the metal ions was taken in a 250 ml conical flask containing 5 g of adsorbent. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature 25°C, pH 6. The pH was adjusted using 1.0M HCl or 1.0M NaOH aqueous solution. The pH of the solution was monitored during the course of the sorption process using a pH meter. The equilibrium was found to have been attained in 90min contact time. After filtration the residual metals in the solution were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (Varian Liberty II ICP-OES), Italy. The removal percentage of metal ions from the solution was calculated using the following relationships as adapted by [15]:

$$\% \text{ metal removal} = (C_0 - C_e / C_0) \times 100 \quad (1)$$

Where: C_0 is the initial metal ion concentration (mg/l), C_e the equilibrium metal ion concentration (mg/l).Adsorption data for adsorbate concentrations are described by Langmuir, Freundlich and Temkin isotherms. Thermodynamic parameters such as change in enthalpy (ΔH˚), change in entropy (ΔS˚) and change in free energy (ΔG˚) were also determined.

Results and Discussion

Scanning electron micrograph (SEM)

Figure (1) displays the microstructures SEM images of SCB. The image showed that, the surface of prepared material was non-smooth and non-homogenous this indicate the possible chances for adsorption of metals on it as stated by [17].

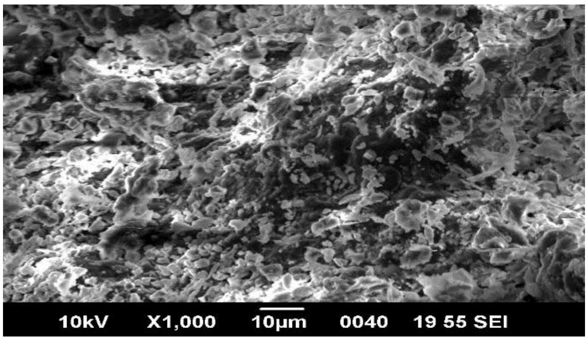

Fig.1. SEM image of SCB

Table 1: Possible assignment of prepared adsorbent from SCB

Functional class	Band position/cm	Intensity	Assignment
Alcohols	3410	Strong	O–H (H-bonded), usually broad
Carboxylic	2930	Weak	–COO–H (very broad)
Aliphatic aldehydes	1650	Strong	C=O (saturated aldehyde)
Aromatics	1420	Strong	C=C (in-ring)
Thiocarbonyl	1200	Strong	C=S
Esters	703	Strong	S–OR

Surface functional group analysis

Table (1) showed FTIR analyses for SCB in order to identify the appearance functional groups. FTIR spectra of SCB showed band at 3410 was assigned to O-H groups which present in phenols, alcohols and carboxylic acids. The region from 3100-3500cm^{-1} attributed to the adsorption bands of hydrogen bond caused by $-NH_2$ and -OH.

Also, absorption bands at 16500 which is a shift of C=O stretching vibration caused by the superposition of C=O in COO^- and C=O in the amide I. The band at 1420 was due to stretching mode of the carbonyls, carboxylic acids, and lactones. The absorption bands at 703 maybe due to ethers, esters, carbonyl groups, and phenol groups [18]. The acidic functional groups like alcohol, and carbonyl groups that found on the surface of SCB enhance the metal adsorption the same results also obtained by [19].

Experimental design for heavy metal removal
Effect of pH

The effects of pH on metals removal were in (Fig. 2). Maximum removal of lead was 92%, Mn 90% and Fe 89% at pH = 6. An increase in adsorption rate was obtained from pH 3 to 6; while, levels of adsorption rate reduced at pH>6 the same results obtained by [20, 21]. Increasing in removal percent by increasing pH solution from3 to 6 may come from the formation of soluble hydroxyl complexes, while decreasing of removal percent above pH 6result from the adsorbent surface that have negative charge from oxygen containing functional groups that causing action between the metal ions and adsorbent [22].

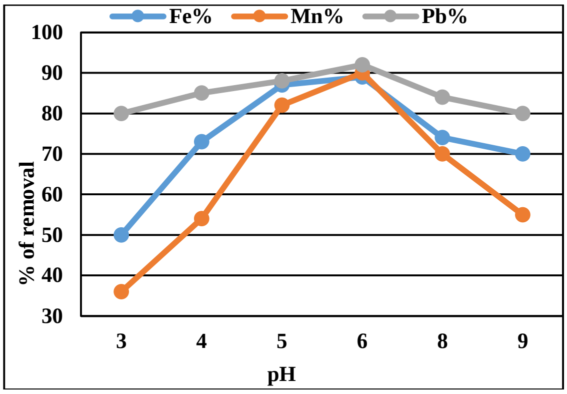

Fig.2: Effect of pH on the removal of Fe,Mn and Pb using SCB adsorbent.

Effect of adsorbent weight

The weight of SCB adsorbent was varied from 0.5 to 6g all the other experimental variables were kept constant pH 6 initial concentration 50 mgL^{-1}, and contact time 90 min. The removal of Fe, Mn and Pb under adsorbent weight effect (Fig. 3) indicated that, the removal percentage decreased with decreasing the adsorbent weight, until equilibrium at 5g. Bhatti *et al.*, [23] showed that, by increasing the adsorbent weight the functional groups on it increased, these groups were necessary during adsorption process in the formation of Vander Waals bonding. This give more possibilities for adsorption of metals and less competition between metals and the binding sites.

Effect of initial metal concentration

The removal of Fe, Mn and Pb using SCB under initial metal concentrations effect. Fig. (4) showed that, the highest removal was recorded for all metals at 50 mg/L and the removal percentage was decreased by increasing the initial concentration of metals.

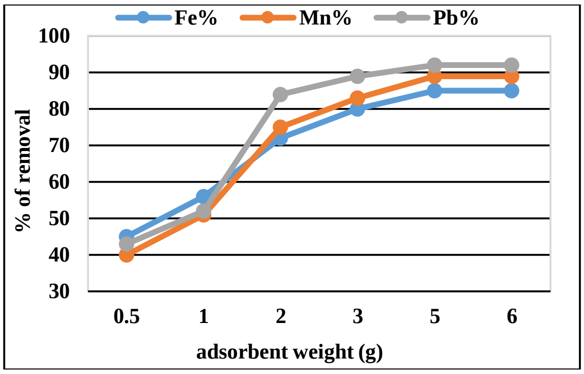

Fig.3: Effect of adsorbent weight on the removal of Fe,Mn and Pb using SCB adsorbent.

This might be come from by increasing the concentration of metal the saturation of the binding sites occurred and un adsorbed metals were left and less binding sites become exist with increasing metal ion concentrations in the aqueous solution [22]. Therefore, concentration of 50 mg/L was considered as the optimum. The best removal was for lead in all metals used and the removal % follows the order Pb>Mn>Fe.

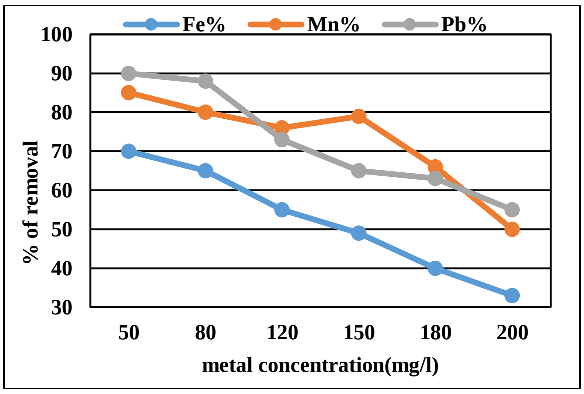

Fig.4: Effect of initial metal concentration on the removal of Fe,Mn and Pb using SCB adsorbent.

Effect contact time

The effects of contact time on heavy metals removal (Fig. 5) gave removal % as 92 for Mn, 88 for Pb and 75 for Fe and the equilibrium was at 90 min. Generally, with increasing the contact time removal percentage was increased, the heavy metals removals follow the order Mn>Pb>Fe. This may give an indication that the adsorption process could happen in a single step [24]. Scott *et al.*, [25] explained that, in the initial stage of the adsorption process, adsorptive ions occupy active surface sites because the surface coverage is low causing higher uptake rate. The surface coverage is increased by time leading to decrease in the uptake rate until the surface becomes saturated.

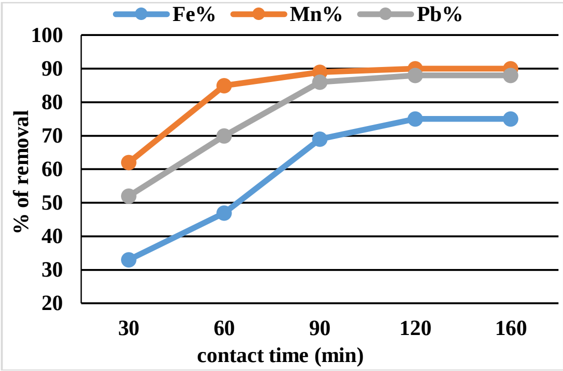

Fig. 5: Effect of contact time on the removal of Fe, Mn and Pb using SCB adsorbent.

Effect of temperature

The range of temperature from 25 to 45 ˚C and optimum parameters are pH, adsorbent dose, initial ion concentration, agitation time and agitation speed were kept at 6, 5g, 50 mg/l, 90 min, 150 rpm, respectively. As seen in (Fig. 6) the effect of temperature on the removal of Fe, Mn and Pb by SCB were 90%, 92% and 89%, respectively. All the metals follow the same trend that, the removal percent increased by decreasing temperature, the results agree with [26] who found that, there is a reverse relationship between the % of removal and temperature.

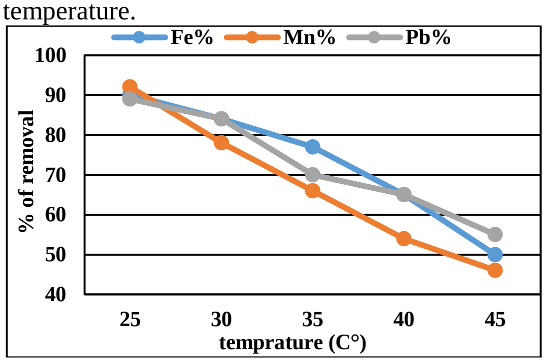

Fig. 6: Effect of temperature on the removal of Fe, Mn and Pb using SCB adsorbent.

Adsorption isotherm investigation

The present study used Langmuir, Freundlich and Temkin models to investigate the adsorption isotherm Fig (7, 8-9). Langmuir isotherm model for Fe, Mn and Pb were explained in Fig. (7), this figure clearly showed that, the adsorption of heavy metals on SCB adsorbent is favorable since R_l lies in the range (0.138-0.525).

Table 2: Langmuir adsorption isotherm constants for the adsorption of (Fe), (Mn) and (Pb) on SCB adsorbents

Heavy metal	Constants	Values
Fe	k_l(L/mg)	0.1238
	$q_{m(cal)}$(mg/g)	3.505
	R_l(L/mg)	0.2121
	r_l^2	0.4
	$q_{m(exp)}$(mg/g)	22.1
Mn	k_l(L/mg)	0.2086
	$q_{m(cal)}$(mg/g)	6.4185
	R_l(L/mg)	0.13778
	r_l^2	0.5725
	$q_{m(exp)}$(mg/g)	26
Pb	k_l(L/mg)	0.0846
	$q_{m(cal)}$(mg/g)	21.93
	R_l(L/mg)	0.283
	r_l^2	0.546
	$q_{m(exp)}$(mg/g)	23.2

Table 3: Freundlich adsorption isotherm parameters for the adsorption of (Fe), (Mn) and (Pb) on SCB adsorbents

Heavy metal	Constants	Values
Fe	k_f (L/mg)	1.158
	$q_{m(cal)}$(mg/g)	5.516
	n (L/mg)	2.0597
	r_f^2	0.876
	$q_{m(exp)}$(mg/g)	23.5
Mn	k_f (L/mg)	1.46
	$q_{m(cal)}$(mg/g)	5.774
	n (L/mg)	2.473
	r_f^2	0.8713
	$q_{m(exp)}$(mg/g)	25.4
Pb	k_f (L/mg)	1.515
	$q_{m(cal)}$(mg/g)	5.708
	n (L/mg)	2.56
	r_f^2	0.862
	$q_{m(exp)}$(mg/g)	23.2

Table 4: Temkin isotherm parameters for the adsorption of (Fe), (Mn) and (Pb) on SCB adsorbents

Heavy metal	Constants	Values
Fe	k_t (L/g)	0.812
	b (kJ/mol)	0.188
	r_t^2	0.962
Mn	k_t (L/g)	0.4899
	b (kJ/mol)	0.073
	r_t^2	0.8363
Pb	k_t (L/g)	0.572
	b (kJ/mol)	0.126
	r_t^2	0.88

Langmuir model suggest the presence of a monolayer adsorbate formed on adsorbent surface and then no more adsorption happen, this used for monolayer adsorption on a surface have a limited identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [27,28]. Freundlich isotherm model for Fe, Mn and Pb metal adsorption on SCB were found in Fig. (8). The results show range of *n* (1.85 -2.64 L/mg) which indicates a favorable sorption process. For Freundlich model a multilayer adsorption happen on a heterogeneous adsorption surface that have different active sites and estimates the intensity adsorption process between the adsorbate and adsorbent [29,30].

From tables (2, 3-4) it is obvious that r_{2T} is higher than r_{2L} and r_{2F} so adsorption process for Fe metal is fitted to the Temkin model (Fig. 9), r_{2F} is higher than r_{2L} and r_{2T} so adsorption process for Mn metal is fitted to the Freundlich model, r_{2F} is higher than r_{2L} and r_{2T} so adsorption process for Pb metal is fitted to the Freundlich model. Dhir and Kumar, [31] reported that, when *n* ranged from1 to 10, this mean adsorption process is good and, when *1/n* less than 1 this indicate easy adsorption for all metals also, high adsorption intensity indicated from higher KF values. So results showed that, the metals were highly adsorbed on the prepared adsorbent as stated by [32].

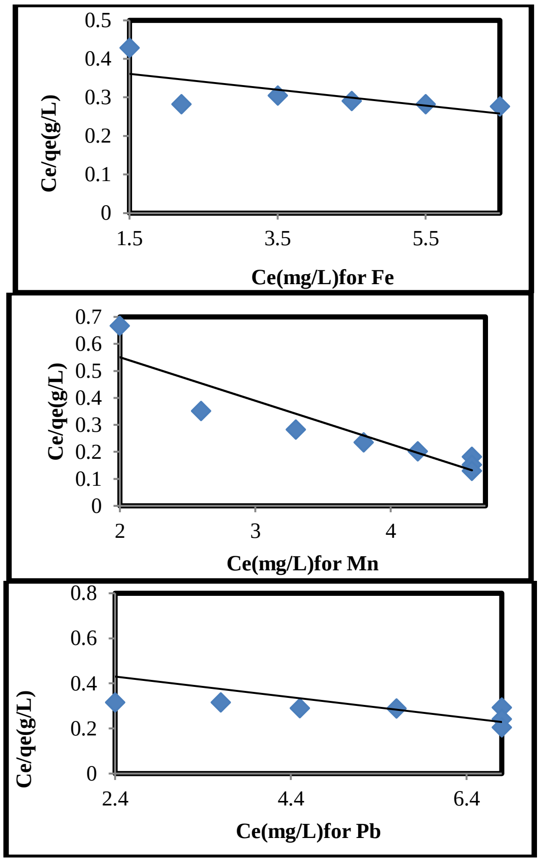

Fig. 7: Langmuir isotherm model for Fe, Mn and Pb metal adsorption on SCB.

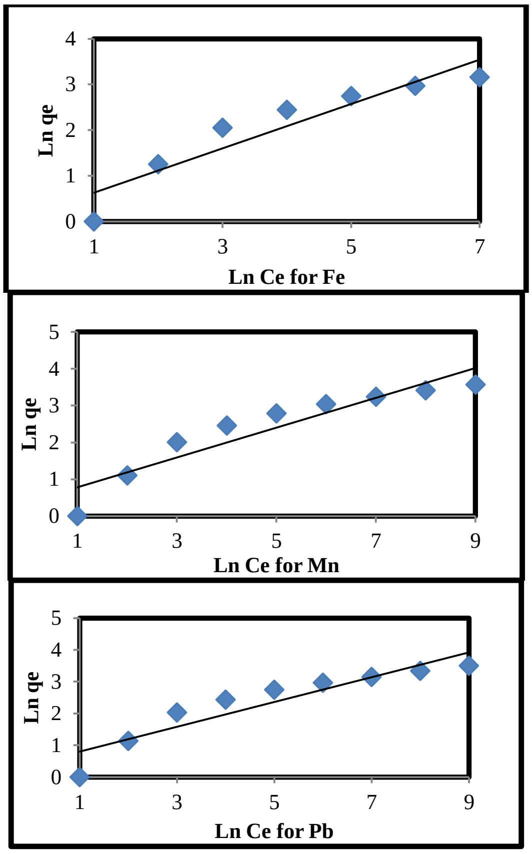

Fig. 8: Freundlich isotherm model for Fe Mn and Pb metal adsorption on SCB.

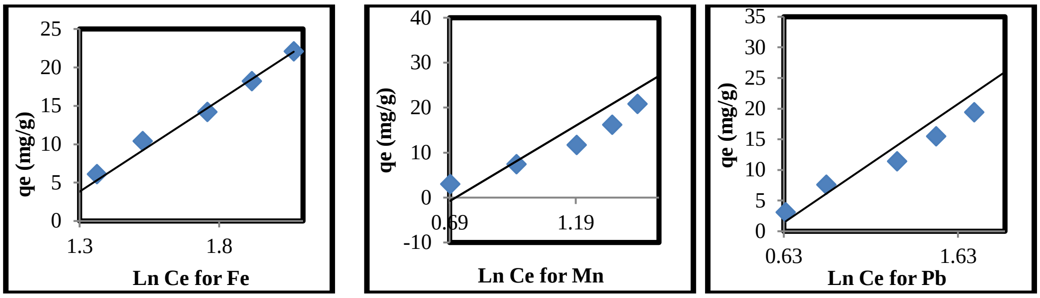

Fig. 9: Temkin isotherm for the adsorption of Fe Mn and Pb metal on SCB.

Thermodynamic Parameter

Thermodynamic parameters change in enthalpy (ΔH°), change in entropy (ΔS°) and change in free energy (ΔG°) were determined by using Van't Hoff equation;

$Ln\ k_c = \Delta S^\circ R - \Delta H^\circ RT$ (2)

Where, k_c is the equilibrium constant (L/g), T is the temperature in kelvin and R is the gas constant (8.314 J/ mol). Plot ln k_c versus 1/T gives a straight line with slope and intercept equal to ($\Delta H^\circ/R$) and $\Delta S^\circ/R$, respectively [33]. The negative values of ΔH° indicate the exothermic nature of adsorption process for heavy metals. The negative value of entropy change (ΔS°) corresponds to a decrease in degree of freedom of the adsorbed species.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$(3)

The thermodynamic parameters values are shown in (Table 5) the negative values of ΔG° indicated that the adsorption of (Fe, Mn and Pb) on SCB is a spontaneous process, whereby no energy input from outside of the system is required. However, the decrease of ΔG°bytemperature increase mean that adsorption at lower temperatures became favorable [33]. As stated by Al Omari *et al.*, [34] the reason for decreasing in adsorption at high temperature is related to when temperature increased, the movement of heavy metals molecules by increasing temperature, causing escape of them to the liquid phase from the solid phase.

Table 5: Thermodynamic parameters for the adsorption of heavy metals (Fe, Mn and Pb) on chitosan and activated carbon particles

Heavy metal	Temp. (˚K)	Ln Kc	ΔG˚ (kJ/mol)	ΔH˚ (kJ/mol)	ΔS˚ (J/mol.˚K)
Fe	298	1.015	-2.37	-17.71	-0.051
	303	0.852	-2.12		
	308	0.695	-1.86		
	313	0.498	-1.6		
	318	0.498	-1.35		
Mn	298	0.85	-1.85	-18.31	-0.055
	303	0.62	-1.57		
	308	0.41	-1.29		
	313	0.28	-1.02		
	318	0.28	-0.74		
Pb	298	0.32	-0.39	-25.21	-0.083
	303	-0.12	0.03		
	308	-0.2	0.44		
	313	-0.49	0.86		
	318	-0.49	1.28		

Conclusion

This work deals with the removal of agriculture wastes by the production of useful biosorbent used for heavy metals removal. The present results found that with increasing in the absorbent dose, contact time and pH value the percentage of removal increased. But when the reaction temperature is raised regularly, it is observed that it negatively affects the metals removal. Also, by applying the adsorption kinetic equations, we found that the best equation explained the adsorption of Fe is Temkin isotherm equation, and in the case of Mn and Pb it was the Freundlich isotherm equation. For thermodynamic parameters ΔG° indicated that the adsorption of (Fe, Mn and Pb) on SCB is a spontaneous process, this means no energy requiredfrom outside of the system.

Declaration of Competing Interest

The author declares that she has no known competing financial interests.

References

[1] Hao Y. and Liu Y. M. The influential factors of urban PM2. 5 concentrations in China: a spatial econometric analysis. J. Clean. Prod112, (2016) 1443-1453.

[2] Alalwan, H. A., Abbas, M. N., Abudi, Z. N., and Alminshid, A. H. Adsorption of thallium ion (Ti+3) from aqueous solutions by rice husk in a fixed-bed column: experiment and prediction of breakthrough curves. Environ. Technol. Innov. 12, (2018a) 1-13.

[3] Abbas, A., Al-Amer, A. M., Laoui, T., Al-Marri, M. J., Nasser, M. S., Khraisheh, M. , and Atieh, M. A. Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Sep. Purif. Technol. 157, (2016) 141-161.

[4] Neoh, C. H., Noor, Z. Z., Mutamim, N. S. A. and Lim, C. K. Green technology in wastewater treatment technologies: integration of membrane bioreactor with various wastewater treatment systems. Chem. Eng. J. 283, (2016) 582-594.

[5] Sud, D., Mahajan, G. and Kaur, M. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - A review. Bioresour. Technol. 99, (2008) 6017–6027.

[6] Abourriche, A., Hannache, H., and Oumam, M. Elaboration of novel adsorbent from Moroccan oil shale using Plackett– Burman design. Chem. Int. 4, (2018) 7-14.

[7] Burakov, A. E., Galunin, E. V., Burakova, I. V., Kucherova, A. E., Agarwal, S., Tkachev, A. G. and Gupta, V. K. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. Ecotoxicol. Environ. Saf. 148 (2018) 702-712.

[8] Alalwan, H. A., Alminshid, A. H. and Aljaafari, H. A. Promising evolution of biofuel generations. Subject review. Renew. Energy Focus 28, (2019)127-139.

[9] Jabbari, V., Veleta, J., Zarei-Chaleshtori, M., Gardea-Torresdey, J. and Villagrán, D. Green synthesis of magnetic MOF@ GO and MOF@ CNT hybrid nanocomposites with high adsorption capacity towards organic pollutants. Chem. Eng. J. 304, (2016) 774-783.

[10] Abbas, M. N. and Alalwan, H. A. Catalytic oxidative and adsorptive desulfurization of heavy naphtha fraction. Korean Chem. Eng. Res. 57, (2019) 283-288.

[11] Noor, N. M., Othman, R., Mubarak, N. & Abdullah, E. C. 2017. Agricultural biomass-derived magnetic adsorbents: preparation and application for heavy metals removal. J. Taiwan Inst. Chem. Eng. 78, 168-177.

[12] Renu, M. A., Singh, K., Upadhyaya, S. and Dohare, R. Removal of heavy metals from wastewater using modified agricultural adsorbents. Mater. Today Proc. 4 (10), (2017) 534-538.

[13] Alalwan, H. A., Abbas, M. N. and Alminshid, A. H. Uptake of cyanide compounds from aqueous solutions by lemon peel with utilising the residue absorbent as rodenticide. Indian Chem. Eng. 62, (2020) 40-51.

[14] Meitei, M. D. and Prasad, M. N. V. Adsorption of Cu (II), Mn (II) and Zn (II) by Spirodela polyrhiza (L.) Schleiden: equilibrium, kinetic and thermodynamic studies. Ecol. Eng., 71 (2014) 308-317.

[15] Rao, M., Parwate, A.V. and Bhole, A.G. Removal of Cr6+ and Ni2+ from aqueous solution using bagasse and fly ash. Waste Manage., 22 (2002) 821-830.

[16] Zanbihi M., Ahmadpour A. and Haghighi A. Removal of mercury from water by carbonaceous sorbents derived from walnut shell .Journal of Hazoudous Materials;167 (2009) 230-236.

[17] Barikani, M., Honarkar, H., and Barikani, M. Synthesis and characterization of chitosan-based polyurethane elastomer dispersions. Monatshefte für Chemie-Chemical Monthly, 141(6), (2010) 653-659.

[18] Kong W., Ren J., Wang Sh. and Chen Q. Removal of heavy metals from aqueous solutions using Acrylic-modified sugarcane Bagasse-based adsorbents: Equlibrium and :inetic. studies. bioresources, 9 (2) (2014) 3184-3196.

[19] Edwin V, A. Surface Modification of Activated Carbon for enhancement of Nickel (II) adsorption. Journal of Chemistry. 5(4) (2008) 814-819.

[20]Fernandez Y., Ulmanu M., Anger I., Maranon E. and Castrillon L. Use of granular bentonite in the removal of mercury(II) cadmium (II) and lead (II) from aqueous solutions, Water Air Soil Pollut., (2010) 239-249.

[21] Wang S. and Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. (2010) 15611-24.

[22] Amuda, O., Giwa, A. and Bello, I. Removal of heavy metal from industrial wastewater using

modified activated coconut shell carbon, Biochem. Eng. J. (2007) 36174-181.

[23] Bhatti, H. N., Mumtaz, B., Hanif, M. A., and Nadeem, R. Removal of Zn (II) ions from aqueous solution using *Moringa oleifera* Lam.(horseradish tree) biomass. Process Biochemistry, .42(4) (2007) 547-553.

[24]Mishra, S. P. and Tiwari, D. Biosorptive behavior of some dead biomasses in the removal of Sr (85+ 89) from aqueous solutions. Journal of radio analytical and nuclear chemistry, .251(1) (2002) 47-53.

[25]Scott, J. A., Karanjkar, A. M., and Rowe, D. L. Biofilm covered granular activated carbon for decontamination of streams containing heavy metals and organic chemicals. Minerals Engineering, 8 (1-2) (1995) 221-230.

[26]Horsfall M. and Spiff, I. Effects of temperature on the sorption of Pb2+ and Cd2+ from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass. Electronic Journal of Biotechnology, 8(2), (2005) 43-50.

[27] Asuquo, E. D. and Martin A.D. Sorption of cadmium (II) ion from aqueous solution onto sweet potato (*Ipomoea batatas* L.) peel adsorbent: characterisation, kinetic and isotherm studies. Journal of environmental chemical engineering,. 4(4) (2016) 4207-4228.

[28] Merrikhpour, H., and Jalali, M. Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite. Clean Technologies and Environmental Policy, 15(2), (2013) 303-316.

[29] Sun, X., Xin, M., Li, M. and Su, S. Preparation of N, N-dilauryl chitosan. Chemical Industry and Engineering Progress. 25(9) (2006) 1095.

[30] Kexi, Z., Jiang, H. W., Xuancong, L. Z., and Zhihao, W. Study on prepration of modified natural rubber latex/chitosan/gelatin composite materials. New Chemical Materials, (5) (2013) 20-32.

[31] Dhir B. and Kumar R. Adsorption of heavy metals by *Salvinia* biomass and agricultural residues. International Journal of Environmental Research. ; 4 (3) (2010) 427-432.

[32] Govindan, S., Nivethaa, E. A. K., Saravanan, R., Narayanan, V. and Stephen, A. Synthesis and characterization of chitosan–silver nanocomposite. Applied Nano Science. 2(3), (2012) 299-303.

[33] Weber, W.J. and Morris J.C. Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division, 89 (2) (1963) 31-60.

[34] Al Omari, M. M., Zughul, M. B., Davies, J. E. D. and Badwan, A. A. Thermodynamic enthalpy–entropy compensation effects observed in the complexation of basic drug substrates with β-cyclodextrin. Journal of Inclusion Phenomena and Macrocyclic Chemistry. 57(1-4) (2007) 379-384.