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Adsorption of Cadmium onto Orange Peels: Isotherms, Kinetics, and Thermodynamics

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Abstract

Batch adsorption of Cd (II) onto orange peel, a residue of the fruits processing industry, has been studied. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated. Equilibrium data fit well with Langmuir isotherm model. The kinetic data were found to follow the pseudo-second-order model. The negative **Δ**H° value indicates the exothermic nature of the adsorption process. Orange peel was shown to be a promising adsorbent for Cd (II) removal from aqueous solutions.

Keywords: Adsorption; Isotherms; Kinetic models; Thermodynamics; Orange peel

Nomenclature

A Constant describing the energy of interaction between solute and adsorbent surface;

β Desorption constant (g/mg) during any experiment;

C_0Initial concentration (mg/l);

CeEquilibrium concentration (mg/l);

K_F & n Freundlich constants;

k_1Pseudo first-order adsorption rate constant (l/min);

k_2Pseudo second-order adsorption rate constant (g/mg. min);

K_D Distribution coefficient ($cm^3.g^{-1}$)

K_LLangmuir constants (L mg^{-1});

k_{id} Intraparticle diffusion rate constant (min^{-1});

MWeight of adsorbent (mg);

q Adsorption capacity,(mg of Cd (II) /g adsorbate);

q_e Adsorption capacity at equilibrium, (mg of Cd (II) /g adsorbate);

q_{max} Maximum adsorption (mg of Cd (II) /g adsorbate);

q_t Adsorption capacity at time t, (mg of Cd (II) /g adsorbate);

R Gas constant (8.314 J/mol/K);

Rc Percent of Cd (II) adsorbed (mg/g);

ReThe removal efficiency of Cd (II) (mg/g);

r^2 Correlation coefficient

TTemperature (K)

tContact time (min);

V Volume of the solution;

α Initial adsorption rate (mg of Cd (II)/g adsorbate. min);

Introduction

Cadmium is one of the toxic heavy metals released to environment from a number of industries such as, electroplating process, metallurgy, pigments, plastic, fertilizers and batteries production. The maximum concentration of cadmium ions in drinking water is 0.003 mg/L according to the World Health Organization [1]. Conventional heavy metal clean-up technologies cover precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultra filtration, solvent extraction, etc.[2]. However some disadvantages of the technologies, such as high cost, sensitive operating conditions and production of secondary sludge [3,4]. Adsorption process has received much interest and become an alternative to conventional precipitation and other techniques, especially for wastewaters that contain low concentrations of metals and its effectiveness [5]. Activated carbon is considered to be a highly effective adsorbent for heavy metal removal from wastewater, but it is readily solubilized under extreme pH conditions [6], and is also very high cost [7]. Low-cost agricultural waste byproducts, such as sugarcane bagasse [8], rice husks [9], sawdust [10], coconut husks [11], and oil palm shell [12], have been investigated to eliminate heavy metals from wastewater. Agricultural residues are usually composed of lignin and cellulose as the major constituents with other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers that facilitate metal complexation resulting biosorption of heavy metal ions[13], from wastewaters. The objective of this research was to investigate the removal of Cd(II) from aqueous solutions by orange peel. The effect of adsorbent dosage, initial metal concentration, contact time, temperature and pH were examined. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been studied.

Materials and Methods

Preparation of adsorbent

Orange fruits were purchased from a local market and peeled

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manually. The peels was washed thoroughly with distilled water to remove the dirt, and dried at 80°C for 24 h, finally crushed and sieved to obtain a particle size of 0.355 mm and used as such.

Preparation of adsorbate solutions

1000 mg/L of Cd (II) was prepared as stock solution by dissolvingthe desired quantity of $CdCl_2{\cdot}2H_2O$ (Aldrich, USA) in distilled water. The required solutions were prepared by diluting the stock solution tothe desired Cd (II) concentrations. The Cd (II) concentrations were determined by an atomic adsorption spectrophotometer.

Adsorption experiments

Batch experiments were carried out to investigate the parametric effects of adsorbent dose, contact time, pH, temperature, and initial Cd(II) concentration foradsorption ontoorange peel. 50mL of different concentrations (50-150 mg/L) of Cd (II) solutions (C_o) with a range of pH values from 2 to10 was transferred in a conical flaskwith a required amount of adsorbent. The solution was agitated at 150 rpm in a thermostatic shaker water bathfor different time (10 to120 min) at different temperature (30, 40, 50 and 60°C). The samples were withdrawn and centrifuged at 5000 rpm for 5 min and the supernatant solutions were analyzed. The pH of the solutions was adjusted with0.1 N NaOH or 0.1 N HCl.

The removal efficiency of Cd (II) was defined as:

$$\mathrm{Re}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

In addition, the adsorption capacity (q) is calculated according to the following equation:

$$q = \frac{C_0 - C_e}{M} \times V \quad (2)$$

Adsorption Studies

Adsorption Isotherms Study

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature [14,15]. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation.

Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by [16]:

$$q_e = (q_{max} K_L C_e)/(1 + K_L C_e) \quad (3)$$

The linear form of the above equation after rearrangement is given by:

$$C_e / q_e = 1/q_{max} K_L + C_e / q_{max} \quad (4)$$

The experimental data is fitted into the above equation for linearization by plotting Ce/qe against Ce. The constants q_{max} and K_L can be determined from the slope and intercept, respectively.

Freundlich isotherm

The Freundlich model [17], is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$q_e = K_F C_e^{(1/n)} \quad (5)$$

Also, the value of n indicates the affinity of the adsorbate towards the adsorbent. The above equation is conveniently used in linear form as:

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

A plot of ln Ce against lnq_e yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants 1/n and ln K_F can be determined from the slope and intercept, respectively.

Adsorption Dynamics Study

The study of adsorption dynamics describes the adsorbate uptake rate and evidently, this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of Cd (II) adsorption on the orange peel was analyzed using pseudo first-order, pseudo second-order, Elovich and intra particle diffusion kinetic models [18,19].

Pseudo-first-order model

The pseudo first order kinetic model [20], was given by equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

Values of k_1 and q_e were calculated from the slope and intercept values of the straight line of plotting log (q_e-q_t) versus t.

Pseudo-second-order model.

The sorption data were also analyzed in terms of pseudo-second order model [20,21],given by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

If the initial adsorption rate, h (mg/g. min) is:

$$h = K2 q_e^2 \quad (9)$$

then Equations (11) and (12) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (10)$$

The plot of t/qt versus t should give a straight line and the pseudo second order rate constant, K_2 and equilibrium adsorption capacity, qe, were calculated from the values of intercept and slope, respectively.

The Elovich model

The Elovich model equation is generally expressed as [19]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta dt) \quad (11)$$

To simplify the Elovich equation, assumed αβt >> t and by applying the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, Equation (9) becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (12)$$

A plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ).

The intraparticle diffusion model

The intraparticle diffusion model is expressed as [16]:

$$R_e = K_{id}(t)^n \quad (13)$$

A linearized form of the equation is obtained as:

$$\log R_e = \log K_{id} + a \log(t) \quad (14)$$

If Cd (II) adsorption fits the intraparticle model, a plot of log R vs. log t should yield a linear relationship with a slope of a and an intercept of log k_{id}.

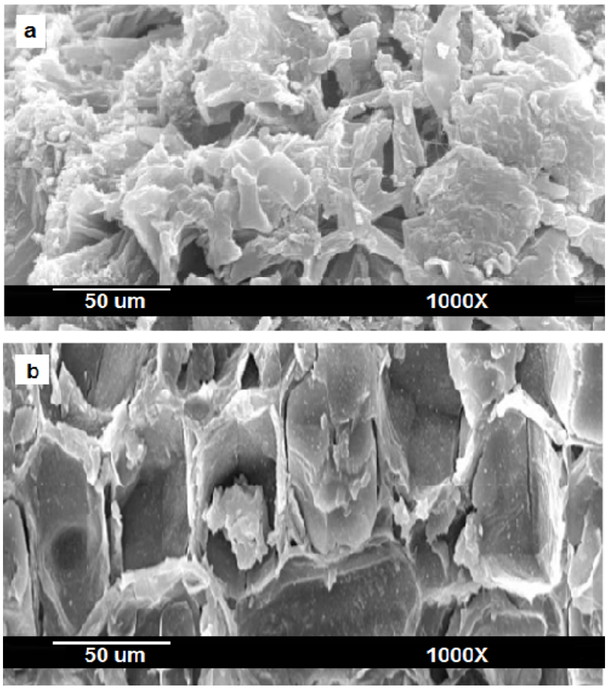

Figure 1: SEM of orange peel (a) before and (b) after adsorption.

Results and Discussion

Characterization of adsorbent

Figure 1a and 1b represent the SEM photographs ofadsorbent before and after adsorption with 1000x magnification. It became apparent from the surface texture ortopology of adsorbent before adsorption that the adsorbent surface isrough, porous and irregular shapes. After adsorption, Figure 1b shows that the metal ion being adsorbed on the adsorbent site. In addition,adsorbent surface was stuffed with Cd (II) ion resulting in loss of surface porosity and roughness.

Adsorption dynamics

Effect of pH: The effect of pH has been studied by varying it in the range of 2-10 at 30°C, 2 hrs, 0.5 adsorbent and particle size of 0.335 mm (Table 1). It was observed that the removalofCd (II) increases with the increase of pHfrom 2 to8. After that, the capacity of adsorption decreases slightly in pH range of 8-10. The highest adsorption efficiency is observed at pH 5. These observations can be explained by the fact that at lower pH values, the competing of H^+ with Cd(II) for the adsorption sites of on orange peel, lead to decreasing the removal percent of Cd(II). But with increasing pH there were fewer H^+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated greater Cd (II) ions uptake by electrostatic attraction. Decreasing in adsorption at high pH may be due to the formation of soluble hydroxyl complexes [22].

Effect of initialCd (II) concentrations and contact time: The removal of Cd (II)ontoorange peel was found to increase with time and attained a maximum value at 60 min. On changing the initial concentration of Cd (II) solution from 50 to 150 mg/l at 30°C, 0.5 g adsorbent, pH 5 and particle size of 0.335 mm. At low concentrations, metal ions are easily adsorbed on vacant sites. Table 1 shows the effect of metal ion concentration on percent removal of Cd (II). As the metal ion concentration increases, the percent removal decreases. Table 1 shows the effect of metal ion concentration on percent removal of Cd (II). As the metal ion concentration decreases, the percent removal increases. This may be due to the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent.

Effect of adsorbent dosage: The adsorption percent at various doses of orange peel from 0.3 to 0.7 g is shown in Table 1. Increasing the adsorbent dose to 0.5 g increase the adsorption percent of metal ions, which is due to the increasing in adsorption sites of adsorbent material resulting from increasing of surface area of adsorbent. However, further increase of adsorbent dosage does not afford exhaustive adsorption of Cd (II). This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles

Adsorption isotherms

The results of this study show that orange peel was effective, in the adsorption of Cd (II) as its removal reached 97.33% at 30°C, pH 5,60 minutes contact time, 0.5 g of adsorbent and Cd (II) initial concentration of 50 mg/l. The Experimental data were applied in the two isotherms (Figures 2 and 3), which results indicate that the adsorption of Cd (II) onto orange peel fits the Langmuir isotherm model because it gives a higher correlation coefficient (r^2= 0.983) value than Freundlich isotherm model (r^2= 0.883), verifying the assumption that the adsorbate molecules could be adsorbed in monolayer coverage on the surface of

Parameter		Removal efficiency (Re %)	q (mg/g)
pH:	2	25.53	1.277
(Condition: 50 mg L^{-1}, mass = 0.5 g, 3 h, 30 °C)	3	84.45	4.252
	4	92.33	4.616
	5	97.33	4.889
	6	97.58	4.875
	7	97.73	4.886
	8	97.70	4.888
	9	89.34	4.457
	10	68.54	3.427
Time (min):	10	49.92	2.460
(Condition: 50 mg L^{-1}, mass = 0.5 g, pH= 5 , 30 °C)	20	56.21	2.811
	30	77.33	3.867
	40	89.50	4.475
	50	93.19	4.659
	60	97.76	4.889
	80	97.71	4.885
	100	97.65	4.882
	120	97.75	4.887
Initial concentration (mg/l):	50	97.76	4.889
Condition: pH= 5, mass = 0.5 g, 60 min, 30 °C)	75	94.29	7.12
	100	90.68	9.36
	125	76.36	9.35
	150	62.28	9.34
Adsorbent dose (g) :	0.3	78.12	4.075
Condition: 50 mg L^{-1}, 60 min, pH= 5, 30 °C)	0.4	91.34	4.567
	0.5	97.76	4.889
	0.6	97.69	4.073
	0.7	97.71	3.489
Temperature (°C) :	30	97.76	4.889
Condition: 50 mg L^{-1}, 60 min, mass = 0.5 g, pH=5)	40	96.50	4.825
	50	95.38	4.769
	60	92.24	4.612

Table 1: Adsorption data of adsorption process.

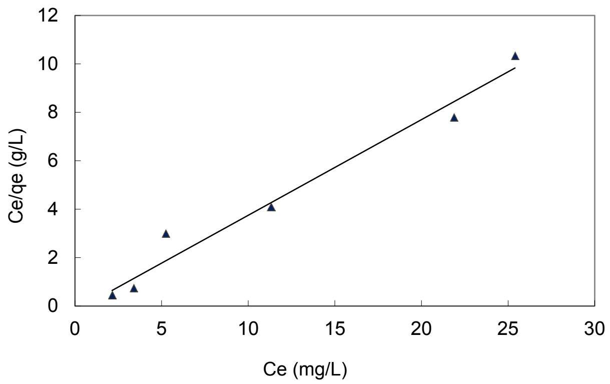

Figure 2: Langmuir isotherm of adsorption process.

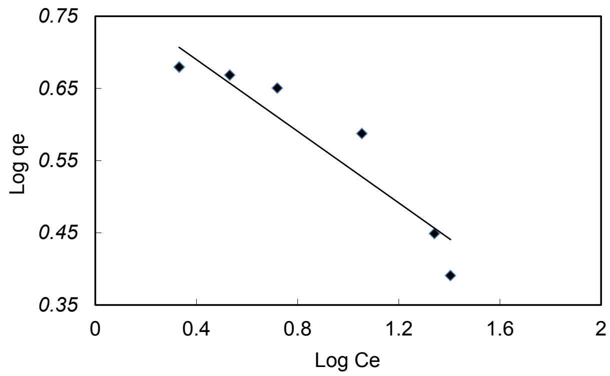

Figure 3: Freundlich isotherm of adsorption of process.

Langmuir constant			Freundlich constant		
K_L	q_{max}	r^2	K_f	n	r^2
0.516	4.90	0.983	6.150	4.032	0.883

Table 2: Langmuir and Freundlich constants of adsorption system.

Experimental q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Elovich model			intraparticle diffusion model		
	K_1 (1/min)	q_e (mg/g)	r^2	q_e (mg/g)	K_2 (g/mg.min)	r^2	β (mg/g)	α (g/mg.min)	r^2	K_{1d} (min^{-1})	a	r^2
15.91	**0.0759**	**6.999**	**0.925**	**4.950**	**0.0971**	**0.988**	**0.759**	**1.231**	**0.901**	**14.79**	**1.366**	**0.805**

Table 3: Adsorption kinetic model rate constants.

the adsorbent. The adsorption constants evaluated from the isotherms with the correlation coefficients are given in Table 2.

Adsorption kinetics

From Table 3 and Figures 4-7 , show that the pseudo second order model is the best fitting model because it gives a higher correlation coefficient (r^2=0.988) than the other kinetic models [pseudo-first-order (r^2= 0.925), Elovich(r^2= 0.901) and intraparticle diffusion (r^2=0.805) models.

Thermodynamic Studies

The effect of the temperature on the adsorption ofCd (II) ions was studied in the range of 30-60°C. The result shows that temperature has anegative effect on the adsorptionofCd (II) onto orange peels. Thermodynamic parameters, such as enthalpy variation (ΔH°), entropy variation (ΔS°)and change in Gibbs free energy (ΔG°),were calculated from the curve relating the distribution coefficient (K_D) as a function of temperature (Figure 8), using the equations [16]:

$$\mathrm{LnK_D} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$\mathrm{LnK_D} = \frac{q}{Ce} \quad (11)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (12)$$

From Figure 8, the values of ΔH^o, ΔS^o were determined from the slope and intercept values of the straight line of plotting ln K_D versus 1/T(K), respectively, (Table 4). Negative value of ΔG^o indicates the feasibility of the process and indicates the spontaneous nature of the adsorption. Decreasing ΔG^o values with decreasing temperature, suggests that lower temperaturemakes the adsorption easier.The negative **Δ**H° value indicates the exothermic nature of the adsorption process. The magnitude of **Δ**H° may give an indication about the type of sorption. Two main types of adsorption are physical and chemical.

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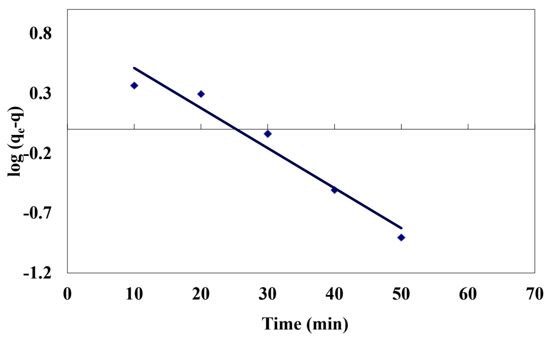

Figure 4: Pseudo-first order model of adsorption process.

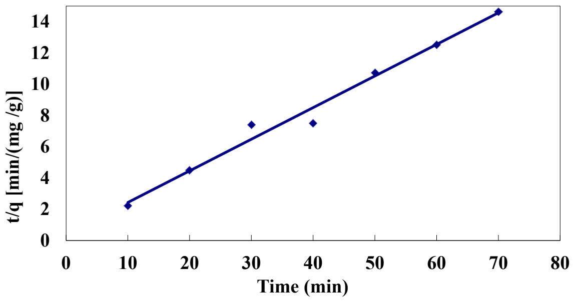

Figure 5: Pseudo-second order model of adsorption process.

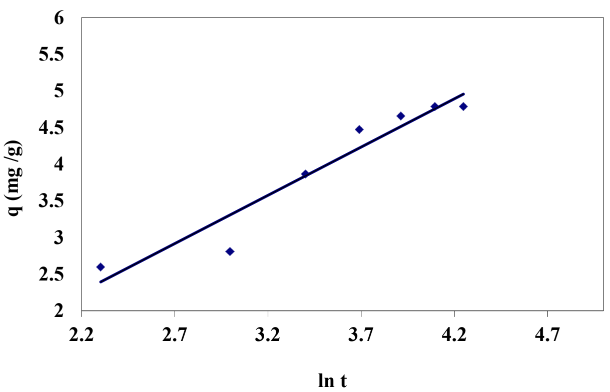

Figure 6: Elovich order model of adsorption process.

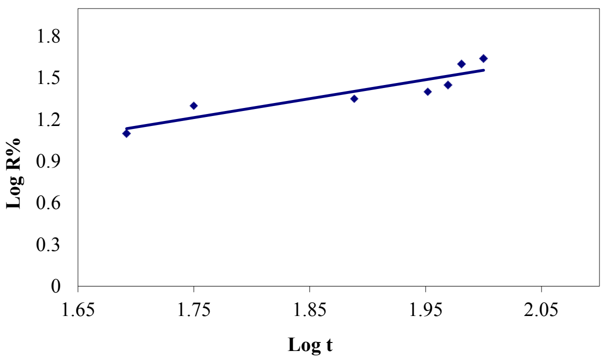

Figure 7: Intraparticle diffusion model of adsorption process.

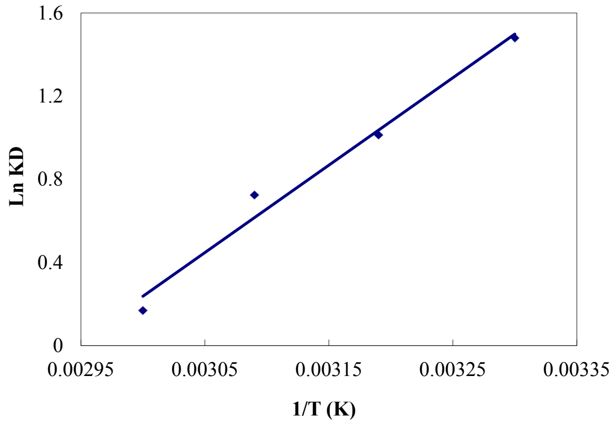

Figure 8: Plot of K_D versus 1/T.

Temperature (K)	LnK_D	Thermodynamic parameters		
		ΔH° (kJ/mol)	ΔS°(KJ/mol.K)	ΔG°(kJ/mol)
303	1.480	-34.935	-0.102	-4.039
313	1.014			-3.009
323	0.724			-1.9989
333	0.170			-0.969

Table 4: Thermodynamic data of adsorption process.

Basically, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1-20.9 kJ/mol, while the heats of chemisorption generally falls into a range of 80-200 kJ/mol [23]. From Table 4, the absolute value of **Δ**H° are 34.935, which therefore indicate that Cd (II) adsorption by orange peelcould be attributed to a physic-chemical adsorption process rather than a pure physical or chemical adsorption process. Negative value of ΔS° indicate a decrease in randomness at the solid/solution interface during the adsorption process while low value of ΔS° indicates that no remarkable change on entropy occurs [24].

Conclusion

Orange peel was effective, as a Cd (II) adsorbent, for which the removal reached 97.33% at 30°C. The highest adsorption efficiency is observed at pH 5. Increasing temperature and initial concentration of Cd (II)lead to decreasing the removal of Cd (II). The Langmuir isotherm model appears to be the best fitting model for adsorption process. The kinetics of Cd (II) adsorption on the orange peelwas found to follow a pseudo second-order rate equation. Thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the adsorption process is spontaneous and exothermic in nature.

References

1. WHO/UNEP (World Health Organization/United Nations Environment Programme (1995) Health Risks from Marine Pollution in the Mediterranean. Part VII. Evaluation of Health Risks from Chemically Contaminated Seafood. Document EUR/ICP/EHAZ94 01/MT01 (2), World Health Organization Regional Office for Europe, Copenhagen.
2. Feng D, Aldrich C, Tan H (2000) Treatment of acid mine water by use of heavy metal precipitation and ion exchange Miner Eng 13: 623-642.
3. Sud D, Mahajan G, Kaur MP (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - a review. Bio resourTechnol 99: 6017-6027.
4. Ahluwalia SS, Goyal D (2005) Removal of heavy metals by waste tea leaves from aqueous solution. Eng Life Sci 5: 158-162.
5. Al-Asheh S, Duvnjak Z (1998) Binary Metal Sorption by Pine bark: Study of. Equilibrium and Mechanisms. Sep Sci Technol 33: 1303-1329

6. Huang CP, Blankenship BW (1984) The removal of mercury(II) from dilute aqueous Solution by activated carbon. Water Res 18: 37-46.

7. Ho YS, Chiang TH, Hsueh YM (2005) Removal of basic dye from aqueous solution using tree fern as a biosorbent. Process Biochem 40: 119-124.

8. Chand S, Aggarwal VK, Kumar P (1994) Removal of Hexavalent Chromium from the Wastewater by Adsorption. Indian J Environ Health 36: 151–158.

9. Srinivasan, K, Balasubramaniam N, Ramakrishna TV (1998) Studies on Chromium Removal by Rice Husk Carbon. Indian J Environ Health 30: 376–387.

10. Ajmal M, Rao RAK, Siddiqui BA (1996) Studies on Removal and Recovery of Cr (VI) from Electroplating Wastes. Water Res 30: 1478–1482.

11. Tan WT, Ooi ST, Lee CK (1993) Removal of Chromium (VI) from Solution by Coconut Husk and palm Pressed Fibre Environ Technol 14: 277–282.

12. Khan NA, Shaaban MG, Hassan MHA (2003) Removal of heavy metal using an inexpensive adsorbent. Proceedings of UM Research Seminar, University of Malaya, Kuala Lumpur, Malaysia, 11th–12th March; Institute of Research Management and Consultancy (IPPP), Ed.; University of Malaya: Kuala Lumpur, Malaysia, 1-5.

13. Hashem MA (2007) Adsorption of lead ions from aqueous solution by okra wastes. Int J PhysSci 2: 178–184.

14. El-Halwany MM (2007) Development of Activated Carbon from Egyptian Rice Hull: Evaluation of Adsorption Properties (Part I). International Chemical Science Conference Sharm El-Sheikh 16-19 April.

15. Muhamad N, ParrJ, Smith DM, Wheathey DA (1998) Adsorption of heavy metals in show sand filters in: Proceedings of the WEDC Conference Sanitation and Water for All Islamabad Pakistan 346-349.

16. El-Halwany MM (2013) Kinetics and Thermodynamics of Activated Sunflowers Seeds Shell Carbon (SSSC) as Sorbent Material. J Chromat Separation Techniq 4: 5-11.

17. Saeed B, Amir L, Seyed JA, Mohammad FR, Akram H (2010) Uranium removal from aqueous solutions by wood powder and wheat straw. J Radioanal Nucl Chem283: 289-296.

18. Romero-Gonzalez J, Peralta-Videa JR, Rodriguez E, Ramirez SL, Gardea-Torresdey JL (2005) Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto Agave lechuguilla biomass. J Chem Thermo 37: 343-347.

19. El-Dien IM, Al-Sarawy AA, El-Halwany MM, Badawy AA (2013) Evaluation of grinding Salix leaves (gsl) as new sorbent material. J Desalination and water treatment 51: 2564-2574.

20. El-Halwany MM (2010) Study of adsorption isotherms and kinetic models for Methylene Blue adsorption on activated carbon developed from Egyptian rice hull (Part II). Desalination 250: 208–213.

21. Monoj KM (2010) Removal of Pb(II) from aqueous solution by adsorption using activated tea waste. Korean J Chem Eng 27: 144-151.

22. Huang X, Gao NY, Zhang QL (2007) Thermodynamics and kinetics of cadmium adsorption onto oxidized granular activated carbon. J Environ Sci (China) 19: 1287-1292.

23. Liang S, Guo X, Feng N, Tian Q (2010) Isotherms, kinetics and thermodynamic studies of adsorption of Cu2+ from aqueous solutions by Mg2+/K+ type orange peel adsorbents. J Hazard Mater 174: 756-762.

24. Abdelkreem M, Dalal ZHusein Removal of strontium from aqueous solutions by adsorption Onto orange peel: isotherms, kinetics, and thermodynamic studies Higher Technological Institute, 6th of October city, 3rd neighborhood, 7th district, Egypt.