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Choosing the optimum conditions of simultaneous adsorption for Lead and Cadmium using Lemon Peels as a adsorbent surface

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ABSTRACT

The study investigated the possibility of removing heavy metal ions (Cd, Pb) from aqueous solutions by using adsorption technology on the citrus peels(lemon), which is a solid waste available in abundance especially in the Syrian coast as well as easy to use at low cost. Work was to determine the optimal conditions for the simultaneous adsorption of each of the ions were determined using (DPASV) method which is characterized by sensitivity and accuracy. The results showed that the optimum adsorption conditions were at PH=5, the time of balance at time = 60 min and the initial concentration is (C0=50-200) ppm. It was noticed by applying adsorption balance for each of Langmuir and Fronlich patterns that Langmuir pattern is the most suitable to express adsorption process for Pb, and Fronlich Pattern Is The Most Suitable To Express Adsorption Process For Cd On Soft And Dry Lemon. The method with its chosen conditions was applied on realistic treated and industrial water waste samples, and it showed a special response as a purification method for aqueous environment.

KEY WORDS: Lead Ions, Cadmium Ions, Water Pollution, Adsorption, Lemon Peels, Water Purification.

1. INTRODUCTION

Heavy metals are considered as a danger on human health even with low concentrations due to its non-decomposition biologically, accumulation in living beings bodies causing different diseases, genetic disorders, harmful environmental effects (Martin, 2009; Kaewsarn, 2001; Yan, 2001; Machida, 2012) as they accumulate in human body after getting exposed to them in different ways (Li, 2011; Zhao, 2010). The industrial development caused the increase of environmental pollution with these metals which caused (air – soil – water) pollution (Florian, 2011), the sources of pollution are variable some of them caused by industrial wastes or fertilizers and pesticides, burning garbage, woods fire or transferring from air to water especially Lead and Cadmium, Arsenic, Copper, and Mercury, most importantly which are found in aqueous solutions and water waste even with low concentration for example (Lead, Cadmium), the study domain (Chakraborty, 2014).

Exposure to Lead even with low concentration causing human health issues (Anemia, nervous system damage, kidney destruction, it also affects children causing mental and physical weakness) (Zhao, 2014). While the danger of Cadmium on human body is due to its almost absent subtraction process and its uniting with some proteins and accumulation in (liver, spleen, kidneys) it also can replace Zinc in some Enzymes which perform important vital functions in human body, therefore they lose their vital potential, and because of the similarity between Calcium and Cadmium it deposits in bones in the form of Cadmium triphosphate which leads in turn to osteoporosis and severe damages in the spine (Mahmood, 2014).

According to the danger of these metals on health and environment and because the pollution types end up on water, environment attention has been paid to the methods of removing these metals from water. Any processing solutions should be done with low cost in addition of low power consumption and small crew. The efforts were dedicated to the development of technologies which can be used such as (electrophoresis reverse osmosis, ion exchange, adsorption, electrolysis using membranes, etc.). The reason which limits the use of these techniques is getting low concentrations of metals, high cost or using chemical additives that increase the pollution rate with solid and liquid materials which complicates the final waste issue (Volesky, 2001).

It was found that using biological systems (bacteria, fungi, algae, yeast) has had increasing attention in removing these metals and that's because the good performance, low cost, as well as they are available with big amounts, unlike (ion exchange, reverse osmosis, etc.) which are expensive in terms of (application or periodic maintenance) (Wang, 2006). Many studies have emphasized the possibility of using crops peels in adsorption of poisoned materials from water (Bailey, 1999). For example bananas peels (Jinlong, 2015), wheat peels (Juliana, 2011), potatoes (El-Ashtoukhy, 2008), pomegranate (Moreno, 2011), almond peels (Estevinho, 2006), rice peels, etc.

The importance of this research comes because it is a scientific addition that adds a new method to the environmental practical methods to get rid of some of heavy metals from aqueous solutions and water waste using lemon peels as a adsorption surface and give a future idea of the possibility of using lemon peels in manufacturing filters to purify water from some poisons to protect the public health.

This research aims to; choosing the optimal terms for the simultaneous adsorption of Lead and Cadmium using adsorption surfaces such as; lemon peels waste these terms include; (acidic conjugate, contact time, initial concentration, competitive ability, adsorption balance) then applying the chosen terms on realistic samples.

2. METHODS AND MATERIALS

Many devices such as:746 Volta metric Analyzer,705 ultraviolet Digester, PH meter, Sensitive analytical balance, and materials such as Standard solutions for Lead, Cadmium, Mercury, acidic solutions, Glacial acetic acid, Nitric acid, Hydrochloric acid, Sulfuric acid are used in our research.

The (differential pulse anodic stripping voltammetry) DPASV is used to evaluate the simultaneous adsorption of Lead and Cadmium ions on lemon peels. Table.1, shows that the analytical optimal terms that were applied to simultaneous determination for lead and cadmium ions using GMFE (Figureite Mercury Film Electrode) in the DPASV.

Table.1. The applied optimal terms to simultaneous determination Pb, Cd using GMFE

Condition	Value
Electrode type	GMFE
Measuring method	DP differential pulse
Quantitative range of survey	- 1200 Mv
Cumulative accumulation	120 Mv
Scanning speed	120 Mv / sec
Pulse capacity	50 Mv
Accumulation time	120 sec
Electrolyte type	CH3COONa / CH3COOH
Electrolyte concentration	0.05 M
Electrolyte PH	4.6
Mercury concentration	25 mg / l

The optimal terms were applied on standard solution for Cadmium and Lead concentration 1ml/g for each one of them, then measuring was done using standard addition method. Volt ampere metric curve was found as figure.1, shows and clarifies that volt ampere metric curve for both ions are perfect in terms of height peaks, separations, and good repetitions in scanning.

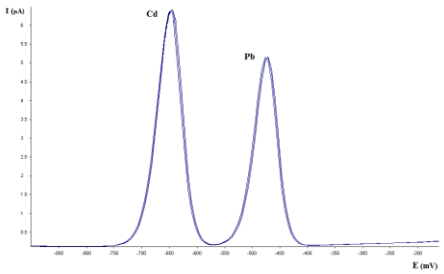


Figure.1. Volt ampere metric curves of standard solution 1mg/l for Lead and Cadmium while applying the optimal chosen terms for Cd, Pb (n=3)

Making of the adsorption surface: Lemon peels were collected from the same type and source, washed with dual distillation water to remove impurities, one part of soft peels was grinded, the other one was dried with desiccator for 24 h at 55 c to get rid of humidity, after that a grinding screening process was made of to get grains with diameter 200 – 500 then was used a adsorption surface without any other treatments (Mingyu Xu, 2013).

Samples preparing: Studied samples were prepared by adding 1 g of soft or dry peels in flask with capacity 50 ml contains sample's solution (Pb, Cd) with initial known concentration with steady vibration speed at laboratory temperature until balance is achieved.

3. RESULTS AND DISCUSSION

Study of the optimal terms of simultaneous adsorption of Cd, Pb ion on lemon peels surface.

Acidic conjugate effect: Acidic conjugate is considered one of the most important factors that affects the metal ions which are in the solution and on the charge of the adsorbent substance (Li, 2007). PH effect on Cd, Pb ions adsorption on soft lemon peels surface was studied in PH domain (2-10) initial concentration of metal ions (100 mg/l), while the other experimental conditions are stable.

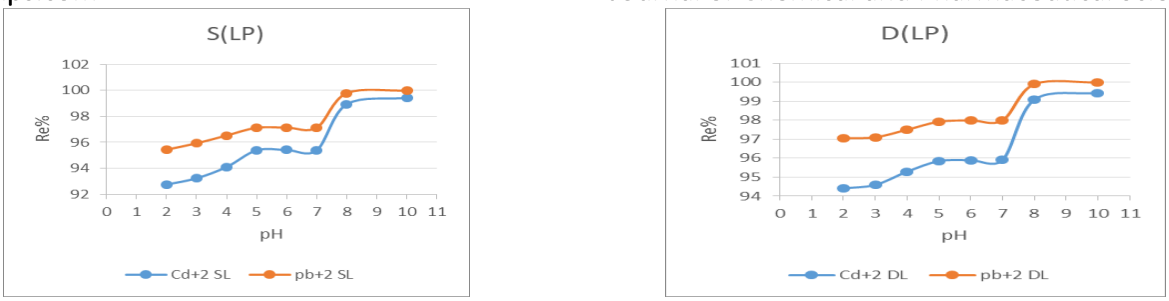


Figure.3. PH effect on Cd, Pb ion adsorption simultaneous on soft S (LP) and dry lemon peels D (LP) surface in order

Figure.3, shows that the highest adsorption rate for Cd, Pb ions compete with Cd ions on adsorption sites in low acidic degrees, adsorption efficiency by using dry peels are higher than when using soft peels. The high adsorption rate of metal ions on lemon peels surface with the increasing of acidic conjugate is due to the decrease of the concentration of hydrogen ions which compete the metal ions on adsorption site, when the decrease of adsorption on the high values of acidic conjugate is due to the formation of liquefied hydroxyl complexes (Zheng, 2008).

Contact time effect: Contact time effect on heavy metal ions (Cd, Pb) adsorption on soft and dry lemon peels surface was studied at initial concentration of metal ions (C_0 = 100 mg/l), PH = 5 while using both soft and dry peels and stabilizing the experimental conditions at time range (30 -180) minutes to make sure to arrive to balance.

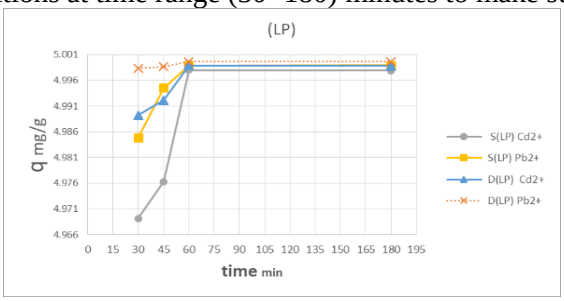


Figure.4. Contact time effect on (Cd, Pb) ions adsorption on soft and dry peels surface

Figure.4, shows that the simultaneous adsorption of (Cd, Pb) ions on both soft and dry peels surface, accelerates initially until it reaches marginal value. That represent balance achieving time between the adsorbed ions on peels surface and the remaining ions in solution.

The high removing rate of metals at first is due to the emptiness of every site on peels surface which is available to metal ions adsorption, then the available centers number decreases, therefore decreasing the adsorption speed.

Initial concentration effect: The initial concentration effect of Lead and Cadmium ions on adsorption rate within concentration domain (50 – 200) mg/l on 1g of soft peels on dry peels powder was studied.

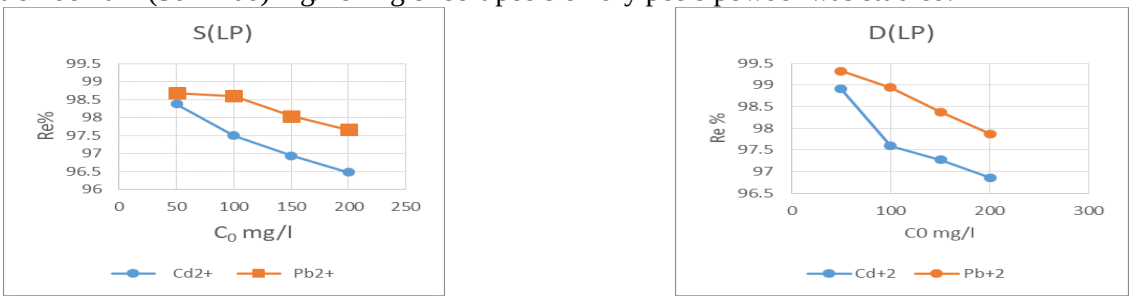


Figure.5. the initial concentration effect on simultaneous adsorption of (Cd, Pb) ions on soft and dry lemon peels surface

Figures shows that the initial concentration of metal ions from 50 to 200 mg / L is associated with a decrease in the percentage of adsorption. There was a decrease in the percentage of removal associated with the increase in primary concentration due to the increase in ionic strength towards the adsorption centers on the surface of the mazze material, but the proportion of residual ions in the solution also increased due to increased primary concentration. This indicates a decrease in the adsorption centers of the mazze material as the ions are increased (Sheela, 2012).

Competitive ability of Pb, Cd ions: The competitive ability of Lead and Cadmium ions during the adsorption on soft lemon peels surface and dry peels powder was studied, the concentration that were taken : (Cd, Pb) (1:1), (1:3), (3:1) and the adsorption rate for each of them on peels surface was studied the results were compared.

Figure.6. The initial concentration effect on simultaneous adsorption of Cd, Pb ions on soft and dry lemon peels

Former information shows that ions compete with cadmium ions on active adsorption sites on lemon peels surface, it was found when preparing concentrations Cd, Pb (1:1) that the percentage of Lead ions adsorption is higher than the percentage of Cadmium ions, we notice that difference between Lead ions adsorption and Cadmium ions at concentration (Cd, Pb) (1:3) is higher than difference between both ions adsorption when the opposite concentration rate was taken Cd, Pb (3:1), we also notice an increase in the percentage of adsorption by using dry peels in compare with soft peels.

Adsorption balance (Langmuir and Fronlich): Many relations are used for characterization of solution adsorption process on the form of mathematical patterns to process the resulting information of adsorption curves. One of the most important relation (Langmuir and Fronlich) which can be written in linear form:

$$\frac{1}{q_e} = \frac{1}{q_{max} b} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (1)$$

$$\ln q_e = \ln K_f + n \ln C_e \quad (2)$$

It's possible figurically to determine both relations constants and characterize the adsorption process of solutions from the linear relations (Azouaou, 2014).

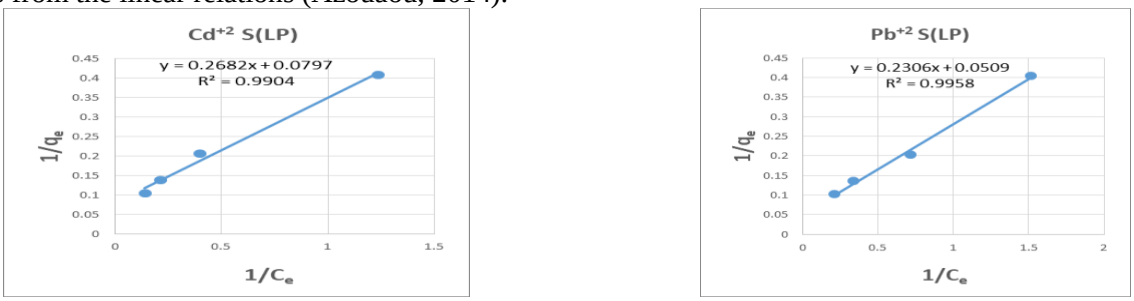


Figure.7. Experimental information processing according to Langmuir pattern at simultaneous adsorption of Cd, Pb ions on soft lemon peels surface

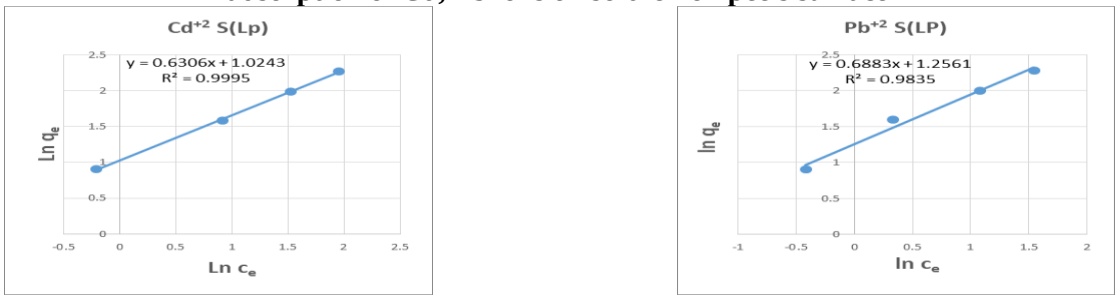


Figure.8. Experimental information processing according to Fronlich pattern at simultaneous adsorption of Cd, Pb ions on soft lemon peels surface

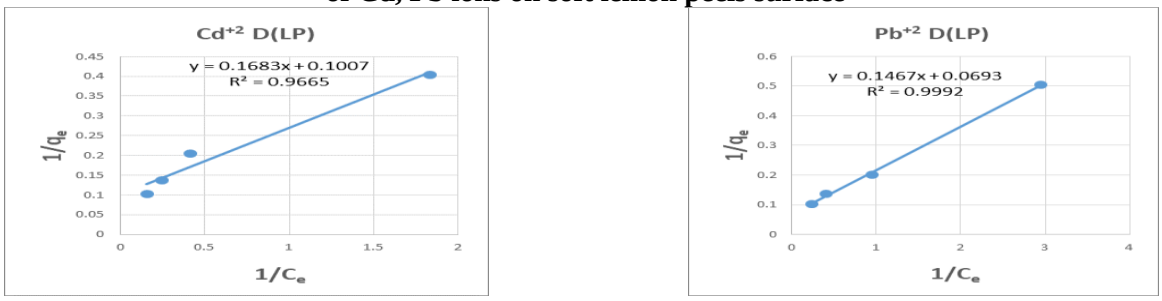
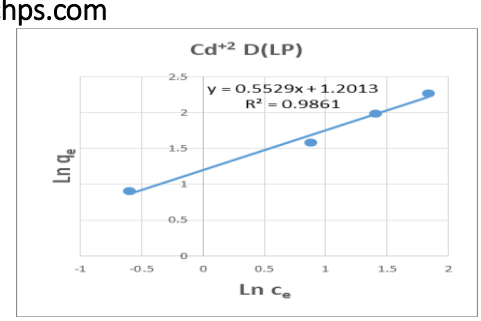


Figure.9. Experimental information processing according to Langmuir pattern at simultaneous adsorption of Cd, Pb ions on dry lemon peels surface



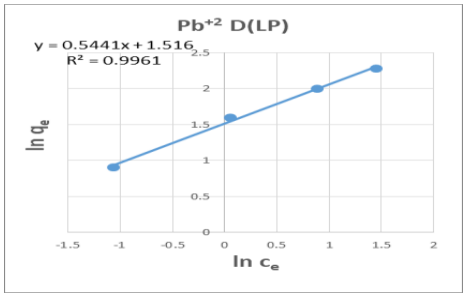


Figure.10. Experimental information processing according to Fronlich pattern at simultaneous adsorption of Cd, Pb ions on dry lemon peels surface

Adsorption curves of Cd, Pb ions on lemon peels surface were studied. Figures. (7, 8, 9, 10) used to evaluate adsorption process and to determine the adsorption type, linear relations were used for both Langmuir (relation 3) and Fronlich (relation 4) were used to draw the adsorption curves and table.2, shows the results.

Table.2. Correlation coefficients and experimental constants for both (Langmuir and Fronlich) at simultaneous adsorption of Cd, Pb on lemon peels surface

Heavy metal ions	Fronlich			Langmuir			
	K_f mg/g	N	R^2	q_{max} mg/g	R^2	R_L	B L/mg
Cd (Cd-Pb)S(LP)	2.785	0.631	1.000	12.547	0.990	0.033	0.297
Pb (Cd-Pb)S(LP)	3.512	0.688	0.984	19.646	0.996	0.059	0.159
Cd (Cd-Pb)D(LP)	3.324	0.553	0.986	9.930	0.967	0.016	0.598
Pb (Cd-Pb)D(LP)	4.572	0.540	0.997	10.384	0.9992	0.015	0.656

Clarified values in table.2, shows that correlation coefficients values R^2 at simultaneous adsorption of Cd, Pb ions on soft and dry lemon peels surface is closer to 1 when using Langmuir pattern compared to R^2 values when using F pattern for Pb ions which means that Langmuir Pattern is the most suitable to express adsorption process for Pb ions and the metal ions adsorption is done on homogeneous surface with monolayer adsorption without any interference between the adsorbed ions and Fronlich Pattern is the most suitable to express adsorption process for Cd Ions multilayered adsorption. N constant value (N > 1) refer to competitive adsorption occurrence. On the adsorption ability centers as for separation factor we find that all of its values are in domain (0 -1) and that shows that the adsorption process on lemon peels surface is reversible process, which means that desorption process of adsorbed ions can be done on soft and dry lemon peels surface.

Removal of lead and cadmium from selected environ-mental water samples: The process of adsorption of Pb^{2+} and Cd^{2+} ions on the surface of dry and soft orange peel was applied within the conditions reached on treated wastewater samples in the rural areas of Lattakia and resulted from three treatment plants distributed in Al-Hara, Habit, Marj Maerban, The samples were collected and the adsorption process was carried out at a laboratory temperature of 25°C with an amount of 0.1 g of Pechher scales with 50 ml of the sample solution at 1 h time, We obtained the results shown in Table.3.

Table.3. Adsorption of Pb^{2+} and Cd^{2+} ions from the selected environmental samples on the surface of the lemon peel using the selected conditions for adsorption

Sampling area	C_0 µg/L	Pb^{2+} S(LP)			Cd^{2+} S(LP)		
		$C_0 - C_e$ µg/L	C_e µg/L	Re%	$C_0 - C_e$ µg/L	C_e µg/L	Re%
Al-Hara Station	34.18	46.71	0	100	34.18	0	100
Habit Station	32.4	32.4	0	100	32.4	0	100
Marj Maerban Station	3.01	42.15	0	100	2.99	0.02	99.336
Tobacco factory	3.57	4.45	0.01	99.97	3.54	0.03	99.160
Sampling area	**C_0 µg/L**	**Pb^{2+} D(LP)**			**Cd^{2+} D(LP)**		
		$C_0 - C_e$ µg/L	**C_e µg/L**	**Re%**	**$C_0 - C_e$ µg/L**	**C_e µg/L**	**Re%**
Al-Hara Station	34.18	**46.71**	**0**	**100**	**34.18**	**0**	**100**
Habit Station	32.4	**39.28**	**0**	**100**	**32.4**	**0**	**100**
Marj Maerban Station	3.01	**42.15**	**0**	**100**	**3.01**	**0**	**100**
Tobacco factory	3.57	**4.46**	**0**	**100**	**3.57**	**0**	**100**

Table.3, shows that all Pb^{2+} and Cd^{2+} ions were removed from treated wastewater samples and industrial wastewater samples from the tobacco Factory using lemon peel. More than 99% of Pb^{2+} and Cd^{2+} ions were removed from treated wastewater samples and sample The industrial waste water produced by this plant has thus proved effective in the purification of wastewater from ions Pb^{2+} and Cd^{2+}.

4. CONCLUSIONS

Form all above we can result that; aqueous solutions can be purified from some of heavy metal using lemon peels (soft or dry) as adsorbent surface because dry peels showed an efficient adsorption more than soft ones; standard simultaneous conditions for both Cd, Pb in aqueous solutions on 1 g of soft or dry peels were determined at (PH = 5, time = 60 min); concentrations that reached 200 ppm for both mentioned ions on surface 1g of dry and soft peels were adsorbed at adsorption rate which was above 95 %.

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