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A Study on the Removal Characteristics of Organic and Inorganic Pollutants from Wastewater by Low Cost Biosorbent

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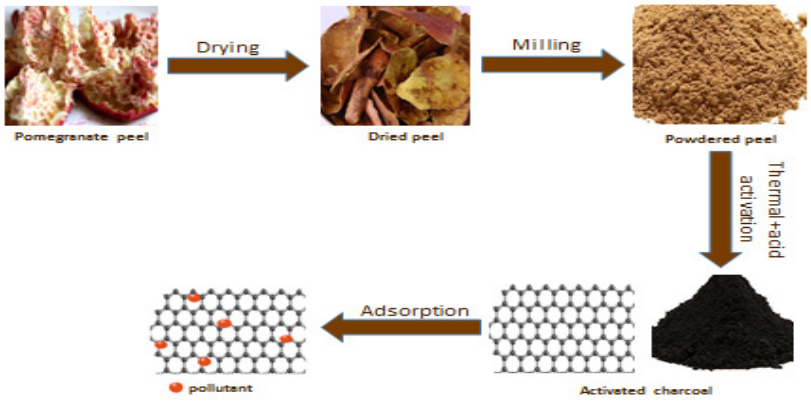

ENVIRONMENTAL pollution has turned out to be one of the serious problems for human, animals and environment at present because of acute toxicities and carcinogenic nature of the pollutants. A lot of organic and inorganic contaminations have been reported in water for example phenol, dyes and heavy metal toxic ions. Pomegranate peels were used as low cost biosorbent to remove organic (phenol& cationic and anionic dyes) and inorganic(Ni^{2+}) pollutants from industrial wastewater. The main goal of this work is to prepare a low cost acid activated carbon from waste pomegranate peels by thermal and acid activation.

Two forms of these peels, dried powder (PP) and Activated carbon (ACPP) were used. ACPP are characterized by different techniques such as IR, XRD, surface area and approximate & elemental analysis. Adsorption process is occurred under some environmental conditions such as pH, temperature, initial concentration, dose of adsorbent and contact time.

The Removal percent for the adsorption of all pollutants were (86.79, 84.15, 83.02, 81.44 %) for MB, Mo, Ni^{2+} ,ph on acid activated carbon.Adsorption capacity of ACPP more than PP. Biosorption procedure was tested on the basis of isotherm and kinetic models . Thermodynamic parameters such as the changes of free energy, enthalpy, and entropy were also calculated. The results showed that the adsorption of dyes, phenol and metal onto surface of ACPP was an endothermic process that could be fitted with the Freundlich adsorption model and pseudo-second order model. The activated carbon could be regenerated and used for 3 adsorption desorption cycle until sorbtion capacity reach to less than 50% than initial sorption capacity.

Keywords: Batch Adsorption, Organic and inorganic pollutants, Biosorbent, Pomegranate peel, Activated carbon, water pollution.

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Introduction

Water pollution becomes among the major pollution contribution in the country. The major sources of wastewater that leads to the water pollution are produced from the textile and dyestuff industries compared to the cosmetic, paper, leather, pharmaceutical and food industries.[1] The industrial activities imply a significant toxin source nowadays, for the most part in regards to addition of heavy metals in the soil.[2] This is due to a amazing increment on the concentrations of those ions in waters which represent a significant source of contamination of the aquatic bodies, especially when it is considered that this type of heavy metals be disseminated via the food chain .[3] Heavy metals discharged into the environment from metal finishing, welding and alloy manufacturing, plating plants and mining because a significant risk to the environment and public health4]].Unlike some organic toxins, heavy metals are not biodegradable and cannot be metabolized as well as decomposed5]]. Dyes are widely utilized in numerous industries, such as in textile, leather, paper, wool, printing and cosmetics. The discharge of wastewater containing dyes into water sources has caused an extreme environmental impact .[6]

As dyeing effluent will exhaust the broke down oxygen content in water and further more inhibit sunlight from reaching to the water sources, some of the dye wastewater is usually poisonous and carcinogenic to human beings [7]. A wide scope of strategies has been embraced for the treatment of wastewater containing dye residues, such as coagulation,ozonation, irradiation, flocculation, electrochemical destruction, membrane filtration, photocatalytic oxidation, ion exchange and adsorption on a solid phase. Adsorption is a low cost and easy friendly method for the removal of toxin dyes [8,9,10].

Biosorption is a physiochemical procedure that happens normally in certain biomass which permits to passively concentrate and bind contaminants onto it cellular structure [11,12]. The plant residues was world widely utilized for waste water treatment for example, peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, peach stones, and numerous others [13,14]. Activated carbon is a black charcoal-like material, which has a well-developed pore structure, which leads to its large surface area; in addition. Activated carbon is commonly used as adsorbent in wastewater treatment [15]. The production of activated carbon from agricultural waste has received much attention from the scientific community as they are renewable, low-cost and environmentally friendly materials [16]. Pomegranate is one of the most popular fruits in the World due to its pleasant taste, high nutritional value, and many medical features. Pomegranate peel is discarded as a toxin residue that can be utilized as a low cost and renewable source of biomass [17, 18].The scope of this work is to prepare low cost biosorbent by modifying pomegranates peel waste for treatment of waste. The production of pomegranate peel based activated carbon (ACPP) through thermal and acid activation has been successfully investigated [19-21].

Experimental Techniques

Materials

Pomegranate peel was obtained from kitchen waste.

NiCl2.6H2O, Methyl orange (MO) with molecular formula C14H14N3NaO3S, Methylene blue(MB) dye with a formula: C16H18N3Cl5 and phenol(Ph) with a formula: C6H6O where obtained from Sigma Aldrich. For pH adjustment throughout the experiment, hydrochloric acid and/or sodium hydroxide solutions were used as necessary. All chemicals and reagent are used as received without any further purification.

Instrumental analysis

FTIR spectra were recorded on Nicolet IS-10FTIR, in the range 400–4000cm^{-1} using KBr pellets. XRD were performed by X-ray diffraction(X pert pro PANalytical) with Cu Kα radiation (λ=0.1542nm) operated at 40kV and 20mA. The textural properties were determined from the N2 adsorption-desorption isotherms at liquid nitrogen temperature (-196^{o}C) using NOVA 3200 S Unite, automates gas sorption analyzer (Quantachrome Corporation) system. A UV/VIS spectrometer model UV-Analytic Jena AG specord 210 plus made by German was used at a wavelength of (190-900) nm at λ_{max} of 664 nm for MB, 464 nm for MO and 270 nm for phenol with a quartz cell of 1.0 cm optical length. The concentration of metal ions remaining in the solution was detected by Atomic absorption atomic absorption (Perkin Elmer model 2380).The pH of the solutions was determined using Jenway 3310 pH Meter. The ash content was determined according to the ASTM D 482 method. The fixed carbon was determined according to the ASTM D 3172 method. The moisture content was determined according to

the ASTM D 3173 method. The volatile matter was determined according to the ASTM D 3175 method. Elemental This technique is used to determine unknown concentration of C,H,N,S. The concentration of CHN was detected by Macro Combustion Analyzer Elementar

preparation of Acid activated charcoal from Pomegranate peel

First step: preparation of powdered pomegranate peel:

Fresh pomegranate peel (PP) was washed to expel dust, dried and cutted, then the cutted pomegranate peel was washed several times with distilled water till no red colored dye was observed. Then it dried in an electrical oven for 24 hours at 90°C. At that point the dried pomegranate peels were grounded and sieved to a particle size 1-2 mm and stored for later use[22].

Second step: thermal activated of powdered peel

The dried and grounded pomegranate peels were thermal activated at 550°C in a furnace for (2 hr) under nitrogen and in the absence of air. After thermal activation, it is treated with HCl solution (0.5 M) to repel ash from thermal activated charcoal.

Third step: acid activation for thermal activated charcoal (ACPP).

Activated charcoal mixed with concentrated hydrochloric acid with 1:4 ratio and refluxed for 6 hr the mixture was filtered and the residual was washed several times with distilled water, then dried in electrical oven at 110 °C for 24 hr and put away in desiccators for later use.

Batch adsorption experiments

This research is carried out to study the factors effecting on adsorption process. These factors included the impact of contact time, solution pH, adsorbent dosage, and temperature. Experimental process was carried out with two forms of adsorbent (PP) and (ACPP) and compare their adsorption removal efficiencies. Batch adsorption methods were used by using knowing weight of adsorbent into separated conical flasks with (25ml) of pollutants (Ph,Mo,Mb, Ni^{2+}) solution of different concentration (25,50,100,300 ppm) and stirred at 250 rpm at different temperature (30°,60,80)) and pH solution (4,7,9).The contact time was determined by stirring 0.25 g from adsorbents with 25ml solution of (100 ppm) of pollutants for different time (15,30,60,120,150)) min. Solution pH was adjusted with 0.1M HCl and 0.1M NaOH. The factor of adsorbent dosage is occurred by adding different weights (0.25, 0.5, 1, 1.5, 2g) of adsorbent. The percentage removal of pollutants in the solutions before and after adsorption was distinguished by utilizing UV-visible spectrophotometer. The adsorption removal percent can be described as[23] :

$$\mathrm{R}emoval(\%) = \frac{(\mathrm{C_i} - \mathrm{C_e})}{\mathrm{C_i}} \times 100$$

The adsorption capacity (Qe) was computed from the equation below[23]: $q_e = \frac{(\mathrm{C_i} - \mathrm{C_e})}{\mathrm{W}} \times V$

Where:-

Ci= the initial feed concentration of pollutants (mg/L)

Ce = the equilibrium concentrations of pollutants in solution (mg/L).

V= the volume of solution (L)

w= the weight of adsorbent (g)

Results and Discussion

Structural characteristics of pomegranate peel Acid Activated Carbon (ACPP)

FTIR

The adsorption on activated carbon was depending on the porosity and the chemical reactivity of the functional groups at the surface of activated carbon. The results in Fig. 1 showed that, FTIR spectrum of the ACPP sample at 3411 cm^{-1} due to the presence of moisture. The –CH stretching in methylene group is detected at 2928 cm^{-1}. The band at 1623 cm^{-1} indicates –N-H stretching in amine compounds. The band at 1353 cm^{-1} due to the presence of methyl group. The band in the region 3500- 3200 cm^{-1} represents the presence of –O-H groups. As there is no evidence of appearance of extra or complexity of bands in the FTIR spectra of acid activated carbon sample it is appeared that acid activation with HCl had not introduced any oxides of chloride.

XRD

From Fig. 2 XRD of the acid (HCl) activated carbon the results showed that the presence of a broad peak between 18 and 22° at 20 ° this give indication about the presence of carbon. The absence of No extra peaks showed in XRD pattern due to the absence of any other x-ray traceable compounds in the activated carbon sample. It is noted that the XRD of hydrochloric

acid which activated sample has not introduced any oxides of chloride at the activation process, as this is evidenced from the absence of additional peaks. This is yet another factor to prove that hydrochloric acid has been completely removed in our sample and also evident that the carbon samples are amorphous in nature.

BET surface area and pore characteristics

The specific surface area and pore characteristics of PP and ACPP samples are represented in Table 1. The results Showed that the BET surface area and total pore volume for ACPP were 542.02 m^2/g and 0.530 cm^3/g, respectively. The average pore diameter for ACPP was 3.24nm. It belongs to the meso pore region according to IUPAC classification. The high surface area and total pore volume of the ACPP was due to intercalation of the HCl with carbon to generate well-developed pores thus creating large surface area and high pore volume by acid activation step which were advantageous for adsorption.

A Proximate and Elemental analysis of ACPP

Table 2 represents a Proximate and elemental analysis of the PP and ACPP samples. The results showed that PP has the highest moisture and volatile matter but with lowest fixed carbon and ash contents. the moisture and volatile content for ACPP less than PP because of the activation process.

Adsorption capacity of PPAC

Effect of pH

The pH of aqueous solution plays a important role in the bio adsorption process due to the fact that H^+ are strongly competing adsorbent. The pH affects the specification of metal ions or dyes and the ionization of surface functional groups.

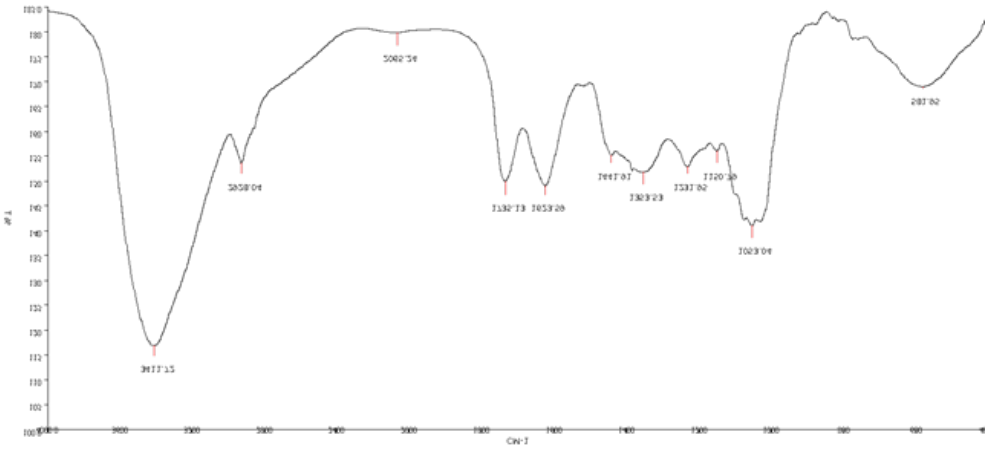

Fig. 1. FTIR of PPAC.

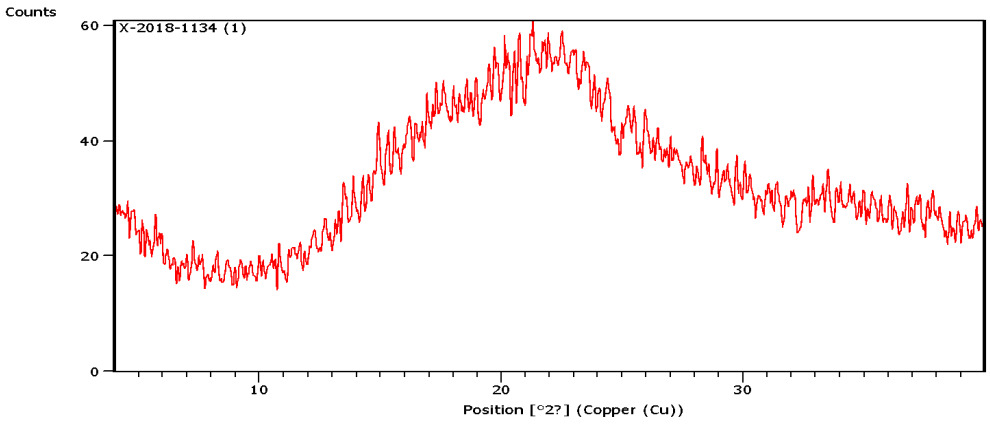

Fig. 2. XRD of PPAC

TABLE 1. Physical properties of PPAC .

Sample	Specific Surface area S (BET) (m^2/g)	Pore volume VP (cc/g)	Pore diameter DV (nm)
PP	8.13	-	-
ACPP	542.02	0.530	3.24

TABLE 2. AProximate and Elemental analysis of ACPP.

Samples	Approximate analysis%				Elemental analysis %			
	Moisture	Volatile	Fixed Carbon	Ash	C	H	S	N+O
PP	6.58	68.36	20.92	4.14	28.16	6.24	0.3	63.26
ACPP	2.39	17.92	76.72	2.97	72.94	4.76	0.06	22.24

The selectivity of pomegranate peel carbon towards pollutants (MB, MO, phenol and Ni^{2+}) as a function of pH in the range (4-9) was measured. Analysis was done using spectrophotometric and chromatographic methods. The data represented in Fig. 3. The results indicate that in case of MB, there is an increase in removal percent with the increase in pH reach maximum value (98%) at pH (9). While in case of phenol the removal percent increase with increase of pH reach maximum value (83%) at pH then it decreased when pH reach (9). In case of MO and $Ni^{2+}$the maximum removal percent reach (85%) at pH (4), then decreased with increase of pH. This fact can be explained by the competition between the surface charge and solution chemistry as two important factors.

Effect of contact time on the adsorption process

The effect of contact time on the adsorption of pollutants (MB, MO Ph and Ni^{2+}) on the pomegranate peel carbon was studied and the data were represented in Fig. 4. The results indicate that the removal percent of pollutants increases as the contact time increases. The adsorption capacity sharply increased during the first 30 min and gradually achieved the equilibrium in 150 min, suggesting that the composite have a high removal percent of pollutants. This can be related to abundant surface active site.

The pollutants adsorption kinetics

One of the most important characteristics in evaluating adsorption efficiency is kinetics. The kinetic of bioadsorption of pollutants onto pomegranate peel carbon was studied using two models. Pseudo-first order and pseudo-second order, models. Concentrations of pollutants and bioadsorbent mass(100ppm,1g) were used at different interval times from (15 to 150 min).

The pseudo-first order equation can be expressed as follow:

The values of K_1 and q_e are calculated from the slope and intercept of the log (q_e–q_t) versus t and they were displayed in Fig. 5 (a) and Table 3. It is clear that the mean correlation coefficient R^2 is (0.953).

The pseudo-second order model can be expressed as equation:

The values of q_e and K_s are calculated from the slope and intercept of t/q_t versus t and the data are represented in Fig. 5 (b) and the parameters listed in Table 3, the mean correlation coefficient R^2 is 0.997. This value was in good agreement much closer to unity than that of pseudo-first order model. This result indicates that the pollutants adsorption on pomegranate peel carbon obeye pseudo-second order kinetics. Thus, these results demonstrated that the adsorption rate was a function of the concentration of free and adsorbed pollutants ions.

Effect of adsorbent dose

The effect of adsorbent amount was performed at a mass range (0.2-2g). The effect of the adsorbent mass usually determined the solid adsorbent's capacity for a given initial concentration of adsorbate in a solution. The results in Fig. 6 showed that with the fixed concentration of pollutants, the percent removal of pollutants ions increases with the increase of the adsorbent weight (pomegranate peel carbon). This is due to greater availability of the exchange

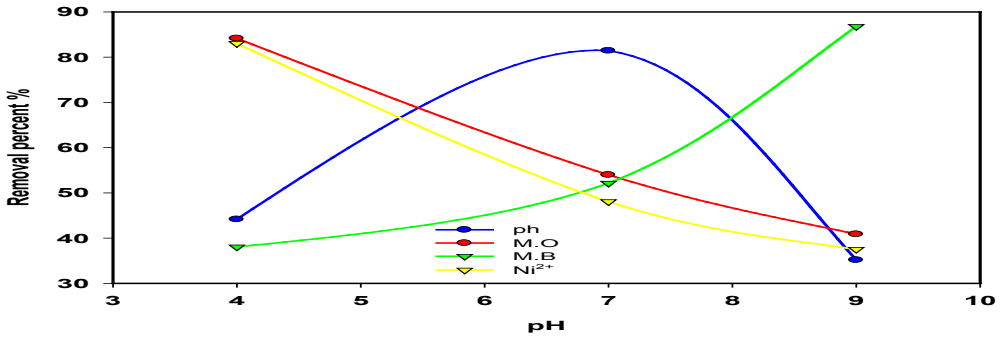

Fig. 3. Effect of medium pH on removal percent of pollutants at initial concentration; 100 ppm, dose; 1g, Temperature; 80°C, and contact time; 150 min.

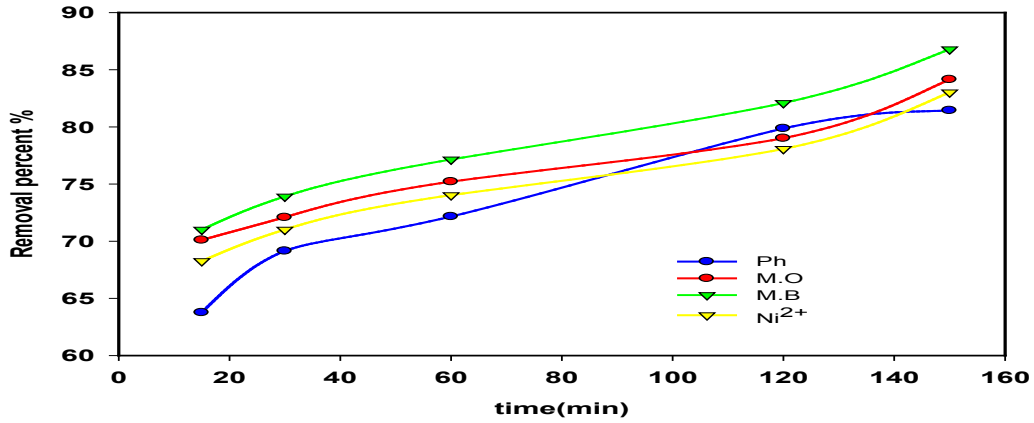

Fig. 4. Effect of time on removal percent of pollutants at initial concentration; 100 ppm, medium pH;4 for (Ni2+,MO), 9 for (MB), 7 for (Ph) Temperature; 80°C and dose;1g

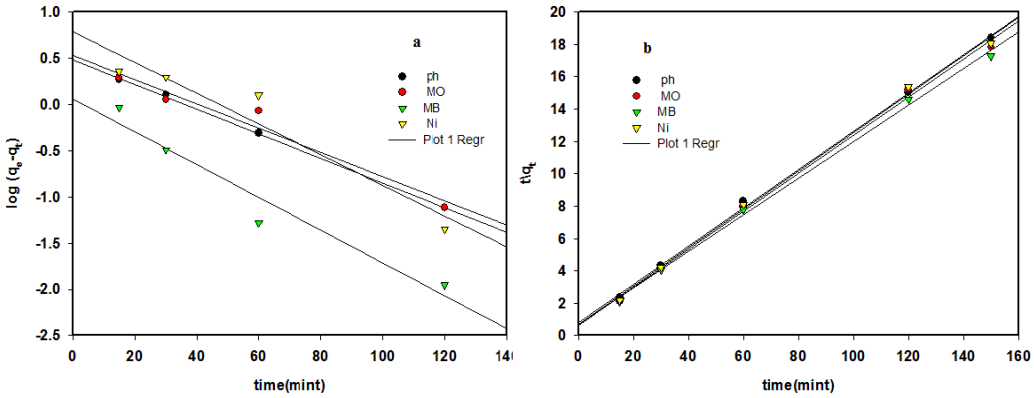

Fig. 5. Adsorption kinetic plots of the pseudo first order (a) and the pseudo second order (b) models.

TABLE 3. Parameter of pseudo-first order and pseudo second order

Rate constant	Parameter	Ph	MO	MB	$^{+}Ni^{\gamma}$
Pseudo first order	k_1 (min−1) $\times 10^{-3}$	0.0306	0.0301	0.0410	0.0383
	Qe,cal (mg/g)	3.0527	3.3564	1.1573	6.1483
	Qe, exp	8.144	8.415	8.679	8.302
	R^2	0.9895	0.95716	0.9452	0.92261
Pseudo second order	k_2 (g/ mg min)	0.0183	0.0216	0.01949	0.02113
	Qe,cal(mg/g)	8.4566	8.5169	8.8354	8.42093
	R^2	0.99873	0.9970	0.99751	0.997201

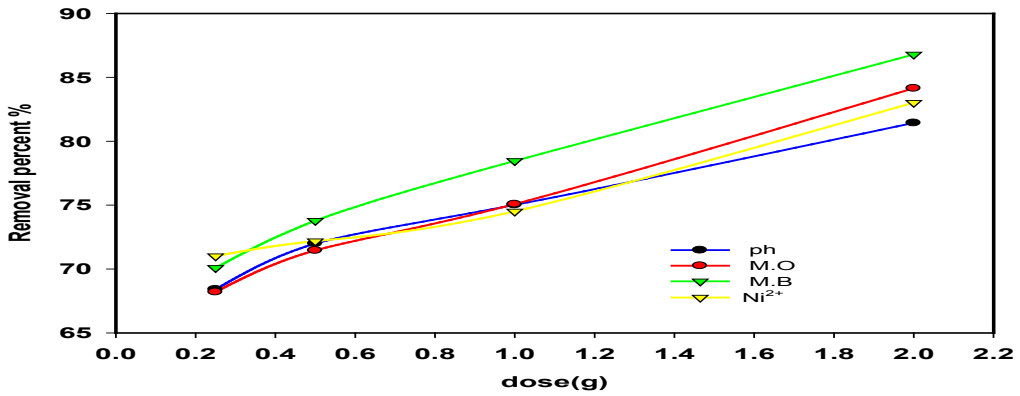

Fig. 6. Effect of adsorbent dose on removal percent of pollutants at initial concentration; 100ppm, medium pH; 4 for (Ni^{2+},MO), 9 for (MB), 7 for (Ph) Temperature; 80°C, and contact time; 150min.

sites or surface area. The removal percent of (MB and MO) reached (85% and 82%) respectively at adsorbent mass 2 g, while phenol and Ni^{2+} ions reached (80, 79%) respectively. The enhancement that was observed in the percent removal of pollutants was principally due to the increase in the active sties on the biosorbent available for adsorption of pollutant molecules.

Effect of pollutant concentrations

Biosorption experiments on the initial concentration of pollutants on pomegranate peel carbon in equilibrium time were conducted for solutions containing 20-100 ppm of two dyes and phenol, (50-300ppm) for Ni^{2+}. The data were represented in Fig. 7. The results indicate that the effect of the pollutants concentration on the percent removal. It is clear that with increasing pollutants concentration the percent removal and the adsorption capacity decrease. At low concentrations, the pollutants are adsorbed to specific sites, while with the increasing of pollutants concentration, the specific sites are saturated and the exchange sites are occupied.

Adsorption isotherm

Analysis of the isotherm data represented in Fig. 8 (a,b), it is important to develop an equation that accurately represents the results and which could be used for design purposes. In this work Langmuir and Freundlich isotherm models were used to describe the relationship between the amount of pollutants (MB, MO, phenol and Ni^{2+}) Adsorbed on pomegranate peel carbon and their equilibrium concentrations.

Langmuir's model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interaction

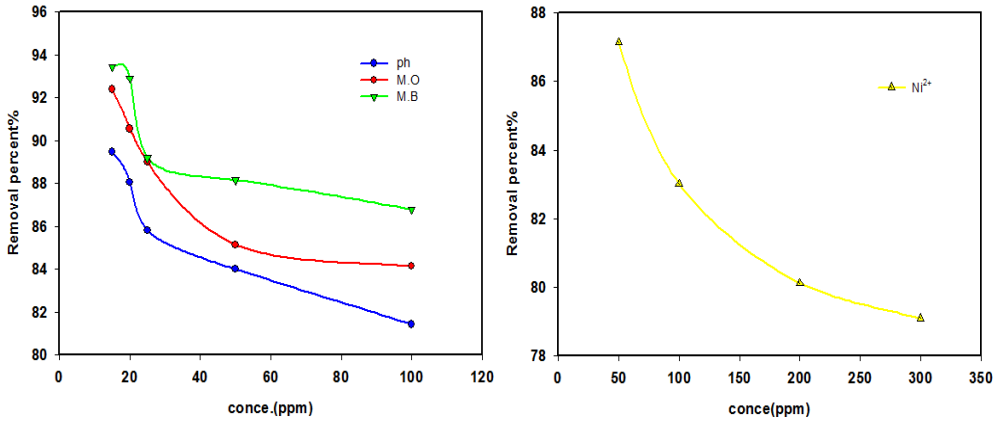

Fig. 7. Effect of initial concentration on removal percent of pollutants at contact time; 150 mint., medium pH; 4 for (Ni^{2+}, MO), 9 for (MB), 7 for (Ph) Temperature; 80°C, and adsorbent dose;1g.

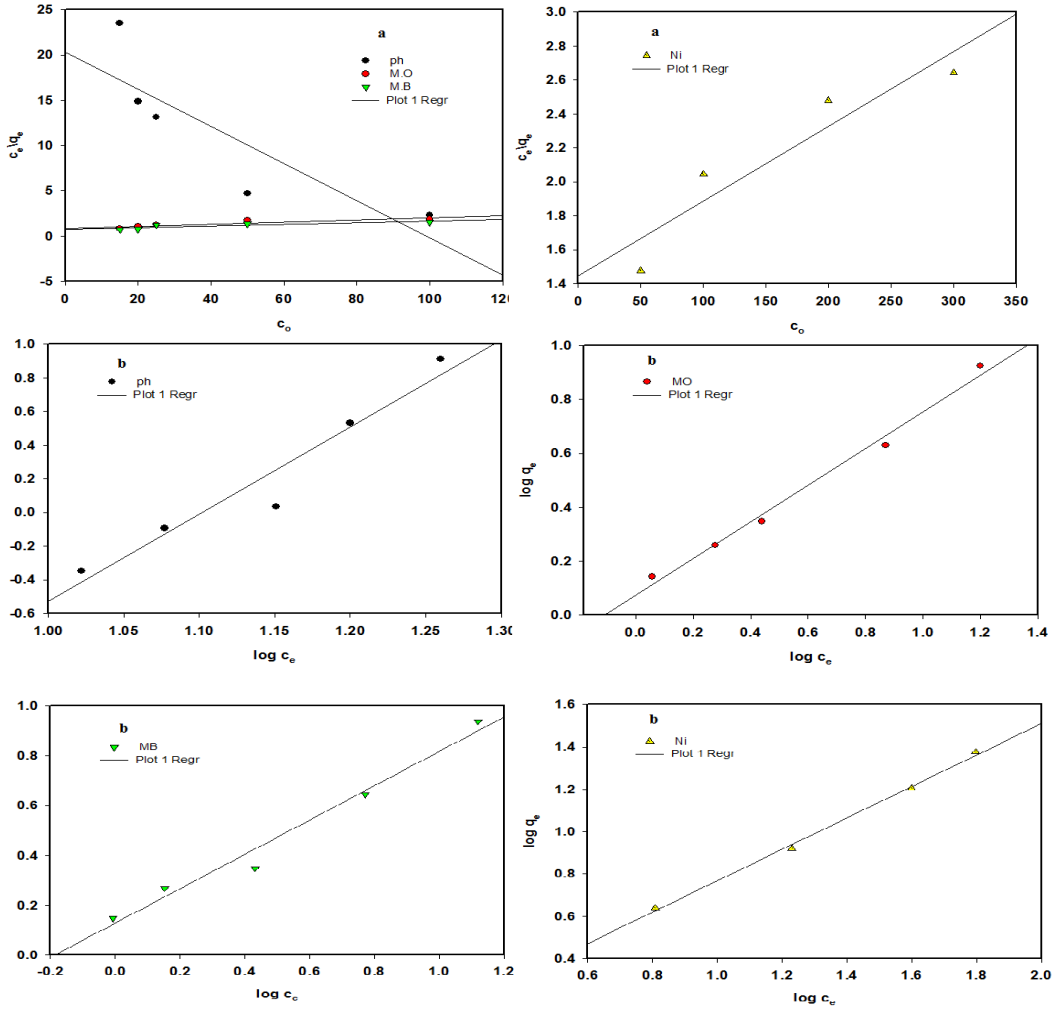

Fig. 8. Adsorption isotherm Langmuir (a) and freundlish (b)

between adsorbed molecules and that the adsorption energy is distributed homogeneously over the entire coverage surface.

Freundlich model is a empirical equation that describes the surface heterogeneity of the adsorbent. It considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich model is represented by:

K_f and 1/n are Freundlich constants depending on the temperature and the given adsorbent-adsorbate couple, n is related to the adsorption energy distribution and K_f indicates the adsorption capacity.

The parameter of Langmuir and Freundlich models are listed in Table 4 for MB, MO, phenol and Ni^{2+}. The values of correlation coefficient, R^2 for the isotherm data are the best for Freundlich model. The values of 1/n are O>1/n<1. Indicating that the pollutants adsorption process is favorable.

Effect of temperature on the adsorption process

The adsorption of fixed concentration of pollutants on pomegranate peel carbon at equilibrium time were conducted in solutions at temperature range 30°-80°C. the data are represented in Fig. 9. The results show that with increasing temperature from 30°80°C the removal percent of pollutants increased, reached to 81.5%, 82%, 83% and 87% for phenol, Ni^{2+}, MO and MB respectively. It is clear that the MB is the best adsorbed. Enhancement of adsorption capacity of pollutants at higher temperatures may be due to the increase in the mobility of the large pollutants ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface.

Thermodynamic studies

In order to confirm the nature of adsorption process, the important thermodynamic parameters, such the standard Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o), changes were calculated according to the following equations

TABLE 4. Parameter of Langmuir and frendlich isotherm modle.

Rate constant	parameter	Ph	MO	MB	Ni^{+2}
langmuir	Qm(mg/g)	4.8614	86.355	0.11548	0.2271
	Ka(L/mg)×10^{-3}	0.01012	0.01349	11.631	3.0481
	RL	0.4970	0.42571	8.5×10^{-4}	3.27×10^{-3}
	R^2	0.723052	0.79889	0.71055	0.87633
Frendlich	KF[mg/g(mg/L)$^{(-1/n)}$]	1.949×10^{-6}	1.1833	1.34517	1.0617
	1/n	5.181	0.68059	0.689	0.7423
	n	0.1930	1.4693	1.4513	1.3471
	R^2	0.9686	0.9897	0.97679	0.9972

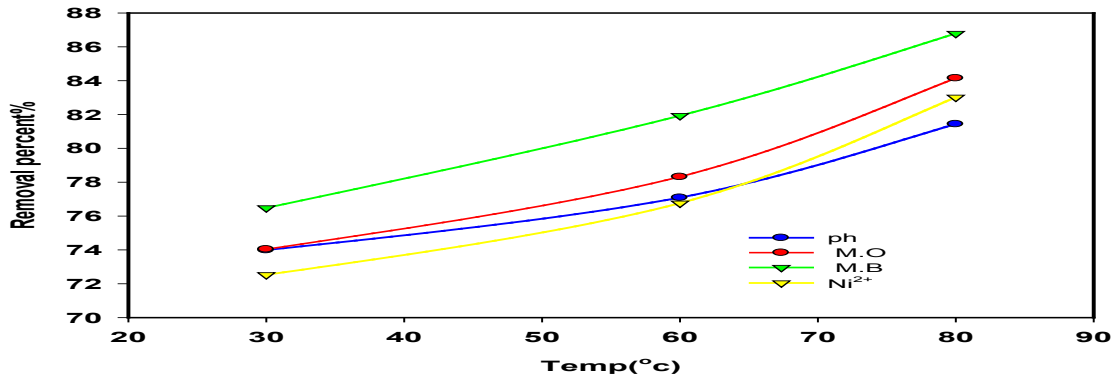

Fig. 9. Effect of temperature on the removal percent of pollutants at initial concentration;100ppm, at contact time; 150min., medium pH; 4 for (Ni^{2+}, MO), 9 for (MB),7 for (Ph) and adsorbent dose; 1g.

$\Delta G^o = -RT \ln K$

$$\text{Ln K} = \frac{\Delta S^o}{R} \frac{\Delta H^o}{RT}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Where,

R is the universal gas constant, T the absolute temperature in Kelvin an K is the equilibrium constant, q_e is the amount of pollutants adsorbed on the pomegranate peel carbon (mg/L),

C_e is the equilibrium concentration of pollutants in solutions (mg/L).

The and ΔS^o of adsorption were estimated from the slope and intercept of the plot of lin K versus 1/T yields respectively. The data are given in Fig. 10 and Table 5. The results indicate that, the negative value of ΔG^o confirms the feasibility of the process and the spontaneous nature of the sorption. The values of ΔH^o were positive, indicating that the sorption reaction is endothermic. The positive values of ΔS^o show the increased disorder and randomness at the solid solution interface during the adsorption of pollutants on the pomegranate peel carbon.

Adsorption of pollutant on PP and PPAC at optimum conditions

Table 6 shows the results of the adsorption of pollutants on ACPP at optimum conditions (concentration 100 ppm, time 150 min., dose 1g ,temperature 30°C and pH according each pollutant). the adsorption of all pollutants are increased in case of ACPP than PP .

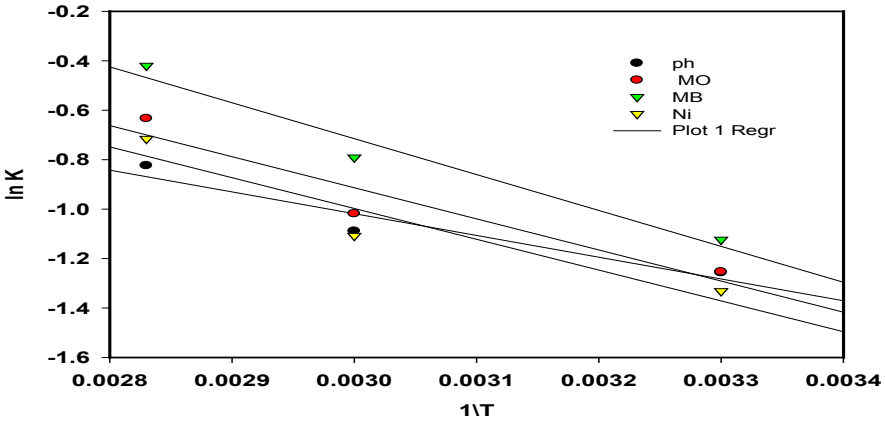

Fig. 10. Thermodynamic of adsorption process of different pollutants

TABLE 5. Thermodynamic parameters of adsorption process:

Pollutants	Temp(K)	Δ G^o (KJ mol^{-1})	Δ S^o $^1J\ mol^{1-}$)-(K	ΔH^o (KJ mol^{-1})	R^2
Ph	303	-11407.24	13491.1	7319.44	0.9197
	333	-11811.97			
	353	-12081.79			
Mo	303	-17667.41	23789.1	10462.07	0.9145
	333	18383.80-			
	353	-9859.587			
MB	303	-21244.01	30270.4	12072.202	0.9643
	333	-22152.11			
	353	-22757.5			
Ni^{2+}	303	-17263.25	22784.0	10359.73	0.90414
	333	-17946.8			
	353	-18402.45			

Adsorption of pollutants on PPAC in mixture system

The adsorption of pollutants in mixture system (MB, MO, Phenol and Ni^{2+}) on ACPP is similar to adsorption in single system, it is affected by pH of solution adsorption was investigated with initial pollutants concentration fixed at (100ppm) for each pollutant and (1g) adsorbent weight the data was represented in Fig. 11. Pomegranate peel carbon (bio-adsorbent) showed more adsorption towards cationic dye (MB), percent removal (41.5 to 82%) with increasing pH from (4 to 9) while the anionic dye (MO), the percent removal decreased from (78.66 to 41.88 %) at pH (9). This can be attributed to the negatively charged surface of bio-adsorbent at elevated pH that attract the positively charged (MB) dye molecule. In case of phenol the percent removal increased with increase pH reach maximum removal (71.6%) at pH (7) then decreased, while in case of Ni^{2+} the percent removal decreased with increase of pH from (77.55 to 35.7 %) removal at pH (9). This result comes in agreement with the results obtained from the single pollutant adsorption experiments but the percent removal is lesser.

Desorption process for different adsorbent materials

From the economic point of view, the adsorbent. could be recycled. Therefore, Regeneration of the adsorbent and recovery of the adsorbed species are significant aspects in a successful adsorption process. Adsorbent that is characterized by better regeneration and better recovery capacity for pollutants (dyes, metal and phenol) are desirable from the cost of usage and recovery of valuable pollutants points of view.

The (MB and Ni^{2+} ions) and (MO and Ph) adsorbed onto the adsorbent could be easily desorbed from the adsorbent by diluted HCl and NaOH solution respectively to recover MB,Ni^{2+}, MO and Ph. The sorption/desorption cycle was repeated for the desired number of cycles until pollutants sorption capacity was less than 50 % of the sorbed pollutant in the first cycle. Figure 12 showed that the activated carbon adsorbent could be recycled for 3 adsorption desorption cycle until sorption capacity reach to less than 50% than initial sorption capacity**.** This means decrease in the percent recovery of the adsorbents adsorption capacity by consecutive regeneration cycles due to the unavoidable losing weight of adsorbent during desorption process as shown in Fig. 12.

TABLE 6. Adsorption of PP and ACPP at optimum conditions:

Sample	Ph	Ni^{2+}	MO	MB
PP	12.93	15.37	17.04	18.81
PPAC	81.44	83.02	84.15	86.79

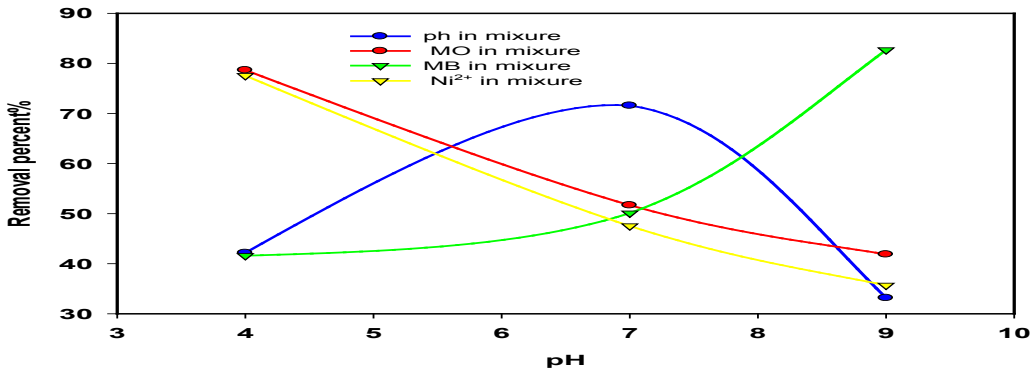

Fig. 11. Effect of medium pH on removal percent of pollutants in mixture at initial concentration; 100 ppm, dose; 1g, Temperature; 80 °C, and contact time;150 min.

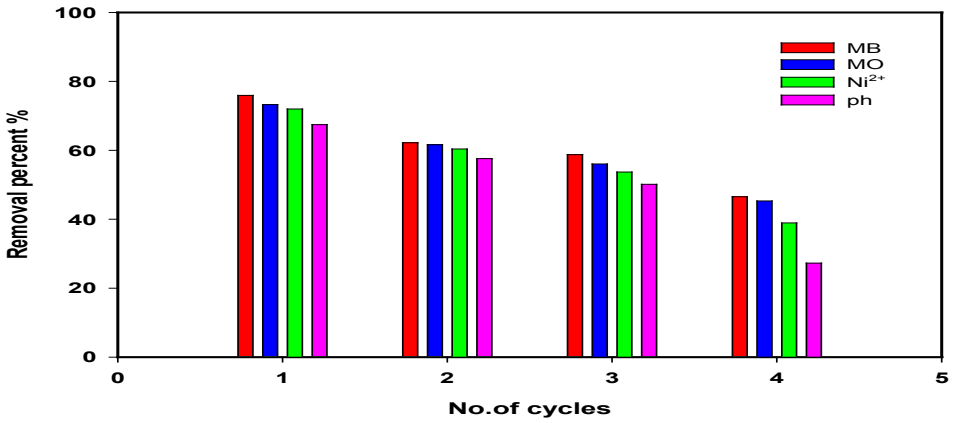

Fig. 12. Effect of adsorption –desorption cycles on adsorption capacities of ACPP in the removal of all pollutants from wastewater

Conclusions

1. Acid activated carbon are prepared by thermal treatment for Pomegranate peel in electrical furnace at 500°C in absence of air for one hour then treated with hydrochloric acid.

2. A prepared adsorbent materials were characterized by FTIR, XRD, surface area, and TGA to verify the functional groups and surface morphology and thermal stability.

3. The optimum conditions for the adsorption of all pollutants (MB, MO, Ni^{2+}, Ph) at contact time 120 min., (9, 4, 4, 7) PH of solution at 1 gm adsorpent dose and 100 ppm for organic and 300 ppm metal ion (Ni^{+2}) concentration with removal efficiency were (86.79, 84.15, 83.02, 81.44 %) for MB, Mo, Ni^{+2}, ph on acid activated carbon.

4. The adsorption equilibrium data found to be in good agreement with Freundlich, adsorption isotherm with high correlation factor R^2 value of the straight lines obtained at various temperature confirm the validity of Frendlich adsorption isotherm for all adsorbent. The adsorption kinetic data was well fitted and in good agreement with psudo-second order for all adsorbent. For acid activated carbon, the positive values of ΔH◦ further confirms adsorption process was endothermic, it will be favorable to carry out removal at high temperature. The thermodynamic parameters were calculated. The negative value of ΔG° imply adsorption is spontaneous process, the decreasing in ΔG° value shows the feasibility of adsorption as the temperature increased indicating less driving force and hence resulting in less adsorption capacity and higher temperature makes the adsorption easier so that the adsorption is more favorable at high temperature. The positive value for entropy ΔS° as refer to increase in randomness at the solid/solution interface during the adsorption.

5. The activated carbon adsorbent could be recycled for 3 adsorption desorption cycle until sorbian capacity reach to less than 50% than initial sorption capacity**.**

References

1. Herrero M., Stuckey D.C., Bioaugmentation and its application in waste watertreatment: a review. *Chemosphere* **140,** 119e128 (2015).

2. Rocha C.G, Zaia D.A.M., Alfaya R.V.D.S., Alfaya A.A.D.S. Use of rice straw as biosorbent for removal of Cu (II), Zn (II), Cd (II) and Hg (II) ions in industrial effluents. *J Hazard Mater*. **166,** 383–388 (2009). doi: 10. 1016/j.jhazmat 11.074 PMID: 19131165 (2008).

3. Wan,M.W.,Kan,C.C.,Buenda,D.R.&Maria,L .P.D.Adsorptionofcopper(II)and lead(II) ions from aqueous solution on chitosan-coated sand. *Carbohydrate Polymers***, 80,** 891–899 (2010).

4. Asmaa S. Hamouda, Sayed A. Ahmed, Nahla M. Mohamed, Mostafa M.H. Khalil ‘’Adsorption of Chromium(Vi) from Aqueous Solution by Glycine Modified Cross-linked Chitosan. *Egypt. J. Chem.* **61**(5), 799 - 812 (2018).

5. Mahmoud G. A., Abdel-Aal S. E., Badway N. A., Elbayaa A. A., Ahmed D. F., A novel hydrogel based on agricultural waste for removal of hazardous dyes from aqueous solution and reuse process in a secondary adsorption*, Polym. Bull.* **74,** 337–358 (2017).

6. Bhattacharya KG, Sharma A Kinetics and thermodynamics of methylene blue adsorption on neem (Azadirachta indica) leaf powder. *Dyes Pigments* **65**(1), 51–59 (2005).

7. Dyes Pigments 56(3):239–249 Okman I, Karagöz S, Tay T, Erdem M Activated carbons from grape seeds by chemical activation with potassium carbonate and potassium hydroxide. *Appl Surf Sci* **293,** 138–142 (2014).

8. Danish M, Hashim R, Ibrahim MNM, Sulaiman O Response surface methodology approach for methyl orange dye removal using optimized Acacia mangium wood activated carbon. *Wood Sci Technol* **48,** 1085–1105 (2014).

9. Wan Ngah W.S., Ariff N.F.M., Hashim, A., & Hanafiah, M.A.K.M.Malachite Green adsorption onto chitosan coated bentonite beads: Isotherms, kinetics and mechanism. *Clean—Soil, Air, Water*, **38**, 394–400.(2010).

10. Aly Al-Sayed, El-Senousy W.M. Al-Herrawy A.Z., Abo Aly M.M., El-Gohary F.A., Membrane Bioreactor Technology for Wastewater Reclamation. *Egypt. J. Chem.* **61**(5), 883 – 896 (2018).

11. Hasan S.H., Srivastava P., Biosorptive abatement of Cd(II)by water using immobilized biomass of Arthrobacter sp.: response surface methodological approach. *Ind Eng Chem Res* **50**(1), 247–258,(2011).

12. Igwe J.C., Abia A.A., Adsorption kinetics and intra particulate diffusivities for bioremediation of Co(II), Fe(II) and Cu(II) ions from waste water using modified and unmodified maize cob. *Int J Phys Sci;* **2**(5), 119–27(2007).

13. Khan, N.A., Ibrahim, S. and Subramanian, P. Elimination of heavy metals from wastewater using agricultural wastes as adsorbents. *Malaysian Journal of Sci.,* **23,** 43-51(2004).

14. Zafar, M.N., Nadeem, R. and Hanif, M.A. Biosorption of nickel from protonated rice bran. *Journal of Hazard Mater.* **143,** 478-485 (2007).

15. Review, Renewable and Sustainable Energy Reviews, **11**, 1966 (2007).

16. Azizian, S., Yahyaei, B., Adsorption of 18-crown-6 from aqueous solution on granular activated carbon: A kinetic modeling study, *Journal of Colloid and Interface Sciences*, **299,** 112-115 (2006).

17. Danish M, Hashim R, Ibrahim MNM, Rafatullah M, Ahmad T, Sulaiman O., Characterization of Acacia mangium wood based activated carbons prepared in the presence of basic activating agents. *Bioresources* **6**(3), 3019–3033(2011).

18. Senthilkumar, T., Chattopadhyay, S.K. and Miranda, L.M., Optimization of Activated Carbon Preparation from Pomegranate Peel (Punica granatum Peel) Using RSM, *Chemical Engineering Communications,* **204,** 238 (2017).

19. Gupta, V.K., Suhas, Application of low-cost adsorbents for dye removale a review. *J. Environ. Manage* **90,** 2313e2342 (2009).

20. Auta, M., Hameed, B.H., Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye, *Chemical Engineering Journal* **171**,502-509(2011).

21. Hassan AF, Abdel-Mohsen AM, Fouda MMG, Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption*, Carbohydrate Polymers*. **102,** 192-198 (2014).

22. Foo K.Y., Hameed B.H., Textural porosity, surface chemistry and adsorptive properties of durian shell derived activated carbon prepared by microwave assisted NaOH activation. *Chemical Engineering Journal* **187**, 53– 62 (2012).

23. Zhuang Li, Lan Li, Danling Hu, Chao Gao, Jinyan Xiong, Huiyu Jiang, Wei Li, Efficient removal of heavy metal ions and organic dyes with cucurbit [8]uril-functionalized chitosan. *Journal of Colloid and Interface Science* **539**, 400–413 (2019).

دراسه عن خصائص ازاله الملوثات العضويه وغير العضويه من المياه العادمه بواسطه مواد ممتزه حيويه منخفضه التكلفه

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يعد تلوث البيئه واحد من اخطر المشاكل التى تواجه الانسان والحيوان والبيئه بأكملها ويرجع ذلك الى طبيعه الملوثات السميه والمسرطنه .لوحظ وجود كثير من الملوثات العضويه وغير العضويه فى المياه مثل الفينول والاصباغ والمعادن الثقيله السامه. لذلك تم استخدام قشور الرمان كمواد ممتزه حيويه منخفضه التكلفه لإزاله الملوثات العضويه مثل الفينول والصبغات وغير العضويه مثل معدن النيكل من مياه الصرف الصناعى.

كان الهدف الرئيسى من ذلك العمل هو تحضير الكربون المنشط حراريا وحمضيا من نفايات قشور الرمان. تم استخدام شكلين من هذه القشور -1 المسحوق المجفف (pp) والكربون المنشط (ACPP) .تم توصيف الكربون المنشط (ACPP) بعده طرق مختلفه مثل X-Ray, IR , Surface area , approximate and elemental analysis

ثم تم دراسه عمليه الامتزاز فى بعض الظروف البيئيه مثل درجه الحامضيه والحراره وتركيز الملوثات وكميه الماده الممتزه وزمن الاتصال .

كانت النسبه المئويه لنسبه ازاله الملوثات كالاتى (86.79 -84.15 -83.02 -81.44) ل كلا من BM و OM وNi^{+2} و Ph على الترتيب .وكانت قدره امتصاص الكربون المنشط اعلى من مسحوق قشور الرمان المجفف.تم دراسه الايزوثرم والكاينتك و الديناميكا الحراريه لعمليه الامتصاص. ووجد ان عمليه الامتصاص تعتبر عمليه ماصه للحراره وتتبع نموذج فريندليش ورتبه التفاعل من الرتبه التانيه الزائفه . تم دراسه قدره الكربون المنشط على اعاده استخدامه مره اخرى ووجد ان يمكن استرجاع الكربون المنشط واعاده استخدامه ل ثلاث مرات حتى تصل قدره الامتصاص الى اقل من 05% من قدره الامتصاص الاولى .