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Preparation of bio-nanoparticles adsorbent derivative from Iraqi date seeds for the removal of pollutants from aqueous solutions

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New type of nanoparticle biomass adsorbent was synthesis from Iraqi date seeds activated carbon (DSAC) and iron oxide nanoparticles (IONPs) under the optimum conditions of temperature, pH and mixture ratio of (FeCl2:DSAC). The final product was characterized for the physical and chemical properties using XRD, SEM, UV, FTIR and color test. Cadmium ion selected in this work as heavy metal; the stock solutions of Cd (II) prepared with concertation of 100 ppm. Four different initial concentrations flasks of cadmium ion prepared (25, 20, 15 and 10 ppm). The adsorption equilibrium experiments of cadmium and led onto nano adsorbent were analyzed by the Langmuir, Freundlich, and the Temkin isotherm models, the equilibrium data fitted well by the Langmuir model with maximum adsorption capacity of 15 mg/g for Cd(II).

Keywords: Date seeds activated carbon; Iron oxide; Nanoparticle's adsorbent; Cadmium; Adsorption.

1. INTRODUCTION

Heavy metals are described as metallic components with a high density in comparison to water [1]. Metalloids, such as arsenic, are present in heavy metals and can cause toxicity at low exposure levels, assuming heaviness and toxicity are related [2]. Environmental contamination caused by these metals has been related to a growing ecological and global public health crisis in recent years. Furthermore, due to an exponential growth in their use in a variety of commercial, farming, residential, and technical uses, human exposure has increased significantly. Heavy metals were also found in various environment including; agricultural, pharmaceutical, domestic effluents, genetic, industrial effluents and atmospheric bases [3].

Many chemical and physical technical methods have been used and developed for the purpose of removal these ions from aqueous solutions. Technologies for the chemical precipitation together with membrane filtration, as well as ion exchange, electrochemical and adsorption. A nanoparticle (NPs) are interested in advancing waste water disposal and the availability of water. For the reduction of different types of contaminants using nano-adsorbents, various nano-adsorbents mainly used in wastewater treatment were categorically addressed, with a special mention of nano-adsorbent regeneration. Nanoparticles (NPs) are a subcategory of nanomaterials that, owing to their peculiar properties and immense applicability, are currently at the forefront of cutting-edge science in almost every field imaginable [4]. Magnetic iron oxide (MIONPs) nanoparticles have gained substantial interest because MIONPs have excellent magnetic properties and low toxicity [5]. Moreover, there is a rich variety of synthetic routes to prepare the most typical oxide form in which IONPs occur in nature, so they have several different morphologies, different shapes, and distributions of particle size. Owing to the inclusion of two cations (Fe^{2+} and Fe^{3+} in their crystal structure), magnetic Fe3O4 and Fe2O3 are a commonly used nanoparticle (NP) having unique properties. Fe2O3 has the structure of corundum, while the other two have the structure of spinel. In the oxidative atmosphere, Fe2O3 and Fe3O4 are metastable, but by heating over 400 ºC they can be oxidized to-Fe2O3. In various areas, such as biomedicine, information technology, and the atmosphere, IONPs have been widely researched for their various applications. IONPs are used in the atmosphere for the elimination or identification of different air, water and soil pollutants by adsorption, photo degradation and photo degradation [6].

2. EXPERIMENTAL

2.1. Preparation of date seeds activated carbon

The date seeds activated carbon prepared according to the previous work, we did [7]. The collected date seeds were washed and dried in an air oven at 70 ºC for 48 h and then crushed and sieved to the desired particle size (2‑3 mm). The resultant sieve cut was carbonized in a stainless-steel vertical tubular reactor placed in a tube furnace at 700 ºC under purified nitrogen (99.995%) flow of 150 cm^3/min for 2 h. The heating rate was fixed at 10 ºC /min. The char produced was then soaked in potassium hydroxide (KOH) solution with an impregnation ratio of 1:3 (Char: KOH wt.%). The mixture was then dehydrated in an oven overnight at 105 ºC and then activated to a final temperature of 850 ºC at heating rate of 10 ºC /min. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide and activation was held for 2 h. The activated carbon was then cooled to room temperature under nitrogen flow of 150cm^3/min. Next the activated carbon was washed with 0.1Mhydrochloric acid and then with deionized water and until the pH of the washing solution reached 6.5‑7.

2.2. Synthesis of date seeds activated carbon - Iron oxide nanoparticles

The dry DSAC were sieved to collect the particle sized with the particle size of (0.5 mm). The collected particles were washed with hexane to remove the oil and subjected to Soxhlet extraction for 3 h. Briefly 50 gm of the prepared DSAC were mixed with 500 ml 50% ethanol in de-ionized water at 70 ºC for 3h, the alcohol was removed from the aqueous solution by rotary evaporator system, then this suspension pass through filter paper (0.22 µm) and the supernatant was cooled to room temperature and stored at 20 ºC. The biosynthesis of date seeds activated carbon (DSAC) and iron oxide nanoparticles (DSAC-IONPS) done by preparation 0.1 M ferrous chloride (FeCl2) by dissolve (12.67 gm) in 1000 ml of deionized water and mixed for 20 min by a magnetic stirrer and stored at 20 ºC until use. DSAC extract considered as good substance for reducing iron salts such as sulfates and chlorides to their oxides. Since DSAC, extract is characterized by high contents of polyphenol compounds so it can be used for the production of IONPs in circumstances of (mixing ferric chloride with activated carbon water extract in 2:1 v/v ratio at pH 3.8) Fe2O3-NPs were obtained with the reduction process. The mixture stirred for 60 min and then allowed to stand at room temperature for another 30 min to obtain colloidal suspension. Mixture centrifuged at 16000 rpm, then, the precipitate washed several times with ethanol and then dried at 45 °C under vacuum to obtain the mixture of Fe2O3-NPs and Fe3O4-NPs. DSAC extract has the best reduction capability against ferric chloride that observed by the external color change.

3. RESULTS AND DISCUSSION

3.1. Ultraviolet-Visible Spectroscopy Analysis

Optical densities of the formed NPs were examined using UV-Vis spectrum with a wave light of 190-800 nm. This analysis was related to the prepared compounds from date seeds activated carbon water extract and iron chloride salt strongly absorbed the radiation at wide range of wave length of ultraviolet -visible spectra ranged from 190-800 nm. The strongest absorbance of radiation at UV was by the DSAC-IONPs at acidic pH, while at the visible spectroscopy all the prepared nanoparticles were slightly different absorbance.

3.2. Adsorption isotherms s

The adsorption data have been subjected to Langmuir, Freundlich and Temkin isotherm models [8-10] summarized in (Table 1). The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 values. The closer correlation coefficients R^2 value to unity, the better the fit. The analysis of the isotherm data was done by fitting them to these isotherm models to find the suitable model that can be used for design purposes. Based on the correlation coefficient, R^2 (0.999) it can be concluded that the adsorption process of our system was demonstrated well by Langmuir isotherm model with maximum monolayer adsorption capacity of 15 mg/g at 30 ^oC.

Table 1 Langmuir, Freundlich and Temkin isotherm model parameters and correlation factors for the adsorption of cadmium onto DSAC-IONPs.

Isotherm models	**Parameters**		
DSAC–IONPs			
Langmuir	q_m (mg/g)	*Ka* (l/mg)	R^2
	15.0	2.95	0.997
Freundlich	K_F (mg/g(l/mg)$^{1/n}$)	*1/n*	R^2
	2.71	0.213	0.902
Temkin	*A* (l/g)	*B*	R^2
	2.35	2.29	0.81

4. CONCLUSIONS

Use the mixing of biomass activated carbon that prepared from biomass agriculture waste with iron chloride under optimum conditions lead to syntheses nano bio adsorbent which highly needed in the environmental field for the purpose of removal pollutants from aqueous solutions. Syntheses of nanoparticles adsorbent have been carried out using date seeds activated carbon and $FeCl_2$. The adsorption of cadmium (as pollutants) onto DSAC-IONPs at 30 ^oC was followed the Langmuir isotherm model according to the R^2 values (0.998) with maximum adsorption capacity of 15.0 mg/g.

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