Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 2, Page 444-451

http://www.jmaterenvironsci.com

Apricot stone- impregnated Fe(III): an efficient, novel and eco-friendly adsorbents for removal of purpurin dye from environmental water samples

Asmaa M. Abdel Rahim[*]

Chemistry Department, Faculty of Science, Minia University, Minia 61511, Egypt

Received 19 Apr 2017,
Revised 04 Sep 2017,
Accepted 13 Sep 2017

Keywords
- ✓ Apricot stone
- ✓ Environmental water samples
- ✓ Impregnation
- ✓ Purpurin

moheyeldin51@gmail.com
Tel.: 01090310922
Fax: 02/086/2369149

Abstract

This work reports the preparation of novel, simple and eco-friendly adsorbents for removal of purpurin dye from aqueous solutions. These adsorbents were prepared through impregnation process for outer shell (AHS) and the kernel (AK) of apricot stone with Fe(III). The developed adsorbents (AHS, AHS-Fe, AK and AK-Fe) are characterized by FT-IR and scanning electron microscopy. The experimental conditions such as pH, adsorbent dosage and dye concentration were optimized for removal of purpurin using these four adsorbents. The maximum adsorption capacity for purpurin on all adsorbents was observed at pH 4.0. It was found that the adsorption percent values of AHS and AK were 20.28 and 10.0 %, respectively which lower than those of AHS-Fe and AK-Fe (97.82 and 98.0 %, respectively). The method was successfully applied for determination of purpurin in environmental water samples using UV/Visible spectrometry at a wavelength of maximum absorbance (485 nm).

1. Introduction

With the increasing rate of industrialization, the releasing of effluents from different industries makes serious threats to several living organisms due to their harmful effects. Synthetic dyes are the most important pollutants of water resources owing to their superior tinctorial strength, simple preparation, cheap and easy availability of raw materials, and good fastness properties [1]. There are many classes of dye include azo, phthalocyanines, aryl-carboniums, polymethines and anthraquinones such as purpurin dye. Purpurin, Fig.1, is an anionic dye with carcinogenic effects that are used in large quantities in dyeing of woven fabrics and wool and cotton textiles and cause many environmental problems [2]. It belongs to the group of anthraquinone dyes; the most durable dyes that cannot be completely degraded by general chemical, physical, and biological processes. Their resistance to degradation is attributed to their complex structures of aromatic rings that afford high physicochemical, thermal, and optical stability.

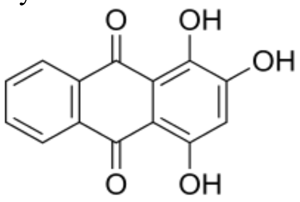

Figure 1: Purpurin structure

In order to control the negative impacts of any dye on living organisms, several techniques and methodologies have been developed for their removal from industry effluents and other water sources. So far, many physicochemical procedures have been developed, including electrochemical degradation, ozonation, oxidation, photocatalysis, membrane filtration, adsorption, and biological treatment [3, 4]. Among these methods, adsorption has been considered as an effective method due to its low cost, simplicity of design, ease of operation without harmful residues, and the possibility of regeneration of the adsorbent. The applicability of adsorption process depends on the adsorbents, which are expected to have high adsorption capacity and available at economical costs [5 – 8]. Currently, many researchers developing simple and novel adsorbents from agricultural waste materials. These waste materials are economic and environment friendly due to their chemical composition, their availability, renewable nature and low cost which viable option for water and wastewater treatment [9]. The basic components of these waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, starch, and contain variety of functional groups [10] as they can complexed with metal ions. These agricultural waste materials have been used in their natural form or after some physical or chemical modification with organic functional groups to increase their efficiency for removal of pollutants [11, 12]. Among these agricultural waste materials, apricot seed which used as adsorbent for removal of many pollutants from water [13 – 15]. It is a Ligninocellulosic materials which can be complexed with metal ions such as Fe(III). To our knowledge, various studies used apricot stone in the form of activated carbon. Moreover, activated carbon is thermally stable, inert and can be used at different ranges of pH [16]. However, the cost of preparation and regeneration of activated carbon is considered high; therefore it considered less economic adsorbent. So, the big challenge in our study is to obtain low cost adsorbent through impregnated with Fe(III). Modification and impregnation techniques were used to increase surface adsorption and removal capacity of adsorbent by simple procedure [17, 18].

So, the main objective of this paper is to develop a novel and simple method for modification of apricot stone through impregnated with Fe(III) which has the ability to bind with purpurin dye. This new adsorbent was used successfully for the removal of purpurin dye from different environmental water samples.

2. Experimental details

2.1. Chemicals

Fresh Apricots were obtained from a local market in Minia, Egypt. Doubly distilled water (DDW) was used throughout all experiments. Ferric chloride ($FeCl_3.6H_2O$), ethanol and purpurin dye were analytical grade from Merck, Germany. ACS reagent grade hydrochloric acid and sodium hydroxide were obtained from Aldrich Chemical Company, USA. Samples of Nile River water (NRW), drinking tap-water (DTW) and ground water (GW) were collected from Minia, Egypt. Also, sample of sea water (SW) was taken from Alexandria, Egypt.

2.2. Preparation of purpurin dye

A stock solution of 0.1 mol/L purpurin dye was prepared by dissolving the appropriate amount of dye in 30.0 mL of 0.1mol/LNaOH and adjusts the volume to 100.0 mL with ethanol. Aliquots of this solution were transferred into 100–mL volumetric flasks and made up to volume with ethanol and DDW (70:30 v/v) to get the final desired concentrations.

2.3. Adsorbent preparation

2.3.1. Preparation of hard shell and the kernel of apricot stone

Apricot stones were opened to obtain the hard shells which contain kernels. The brown crust of kernel was removed to obtain the white part (kernel). The woody hard shell and kernel were cut and washed with DDW and air dried. They were ground in a laboratory mill and sieved to small particle-size fractions using a conventional sieve. Then, the small particles of both hard shell (AHS) and kernel (AK) was washed with DDW and left to dry in an oven for 1h at 60^{o}C.

2.3.2. Impregnation of apricot hard shell and kernel with Fe(III)

To increase the uptake of Fe(III), the AK was loaded with vitamin C (AK-C) with weight ratio of (1:0.5 w/w). Then, 500.0 mg of each AHS and AK-C was soaked for two days in 50.0 mL of 0.5 mol/L $FeCl_3.6H_2O$ solution (its pH was adjusted to 3.5 by adding drops of 1.0 mol/L NaOH and 1.0 mol/L HCl). Then this mixture was filtrated and washed with DDW in order to remove the residues of $FeCl_3$ as the filtrate being colorless. The modified phase was left to dry in an oven at 60 ◦C for 1h. A confirmation that the modification process has successfully achieved, it was found that the color of each adsorbent (AHS-Fe and AK-Fe) was changed from brown to black one for AHS-Fe and from white to brown one for AK-Fe as shown in Fig. 2.

2.4. Adsorbent characterization

The surface functional groups of AHS and AK before and after impregnation with Fe(III) were analyzed by Fourier transform infrared (FT-IR) spectroscopy (410 JASCO, Japan). The surface morphology of the adsorbents was characterized using scanning electron microscopy (JSM-5400 LV JEOL, Japan).

2.5. Studies on point zero charge (pH_{zpc}) of adsorbents

In pH_{zpc} determination, 200.0 mg of each adsorbent (AHS, AHS-Fe, AK and AK-Fe) was added to 50.0 mL of 0.01 mol/LNaCl and its pH was adjusted in the range of 2.0 – 12.0 by adding appropriate volumes of 1.0 mol/L HCl or 1.0 mol/L NaOH [19]. These flasks were kept for 48 h and final pH of the solution was measured by using Fisher Scientific Accumet pH-meter (Model 825, Germany). Graphs were then plotted for pH_{final} versus $pH_{initial}$.

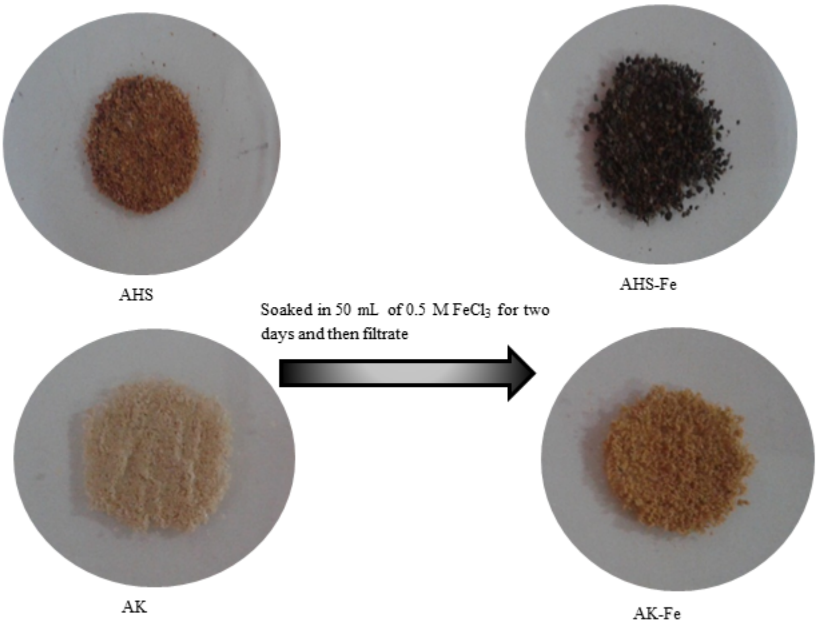

Figure 2: Impregnation of AHS and AK adsorbents with Fe(III)

2.6. Batch adsorption experiments

The adsorption experiments were carried out using batch method. Different parameters such as effect of pH, dye concentration, adsorbent amount and contact time were studied. Definite weight of each adsorbent (AHS, AHS-Fe, AK and AK-Fe) was added to 50.0 mL of 1.0×10^{-3}mol/L of purpurin dye. Different additions of 1.0 mol/LNaOH or 1.0 mol/L HCl solutions were used for justifying the pH values before adding the adsorbent. The solution was then shaken at different time intervals at room temperature to attain equilibrium. Subsequently, these solutions were filtered out by using filter paper. The filtrate after adsorption process was analyzed using UV/visible spectrometer by recording the absorbance changes at a wavelength of maximum absorbance for purpurin dye (485 nm). The amount of dye adsorbed on the adsorbent surface was calculated from the concentrations difference in solutions before and after adsorption. All the adsorption experiments have been carried out in triplicate. The adsorption percentage of the dye adsorbed was calculated using the equation:

$$\% \text{ Removal (adsorption)} = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

whereC_i is the initial concentration of dye and C_f is its final concentration.

2.7. Removal of purpurin dye from environmental water samples

Different water samples drawn from Nile River water (NRW), drinking tap-water (DTW), sea water (SW) and ground water (GW) were collected and stored in clean polyethylene bottles. The water samples were filtered before the analysis to remove any insoluble substances. The pH of the water samples (DTW, SW, GW and NRW) spiked with 2.0×10^{-4} and 1.4×10^{-4} mol/L purpurin dye was adjusted to 4.0 with additions of 0.1 M HCl solution. Then appropriate weight of each adsorbent (20.0 and 30.0 mg of AHS-Fe and AK-Fe, respectively) was added to 50.0 mL of each water sample and shaking for 30 min. Each filtrate was taken and the concentration of dye was determined by UV/visible spectrometer using the previous procedure as described above.

3. Resulats and Discussion

3.1. Characterization of adsorbent

3.1.1. FT-IR

The FT-IR spectra of AHS, AHS-Fe, AK and AK-Fe adsorbents produced are shown in Fig. 3 (a and b). The AHS and AK spectra show three main absorption bands for 3300-3500 cm^{-1}, 2800-3000 cm^{-1} and 1700-1000 cm^{-1}. The band at 3420 cm^{-1} is attributed to the O–H stretching of the hydroxyl group. The bands at 2925 and 2854 cm^{-1} represent C–H interaction of alkyl groups and $-O-CH_3$, respectively. The peak at 1744 cm^{-1} is attributed to the carboxylate stretching. The peak at 1654 cm^{-1} is expected either due to amide group (N–H) or carbonyl group. The peaks at 1429 and 1051 cm^{-1} may be due to O–H from either hydroxyl or carboxylic group and C–O of alcohol group, respectively [20–24]. After modification process, in the case of AHS-Fe and AK-Fe, the peaks at 3420, 2925, 2854 and 1744 cm^{-1} are decreased in the intensity. The peak at 1654 cm^{-1} is increased in the intensity and shifted to 1642 cm^{-1}. Also, the peak at 1051 cm^{-1} was shifted to 1035 cm^{-1} and increased in the intensity. The changes in the absorption peaks generally emphasize that the modification process with Fe(III) taking place on the surface of the AHS and AK.

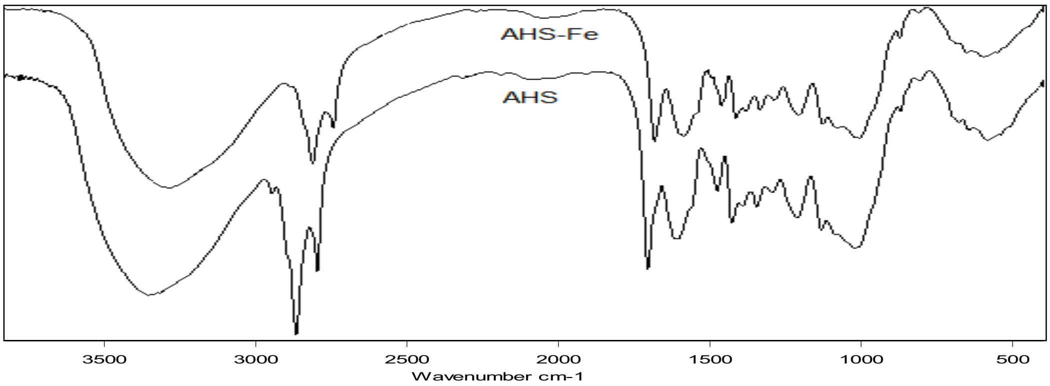

Figure 3(a): FT-IR spectra of AHS, AHS-Fe adsorbents

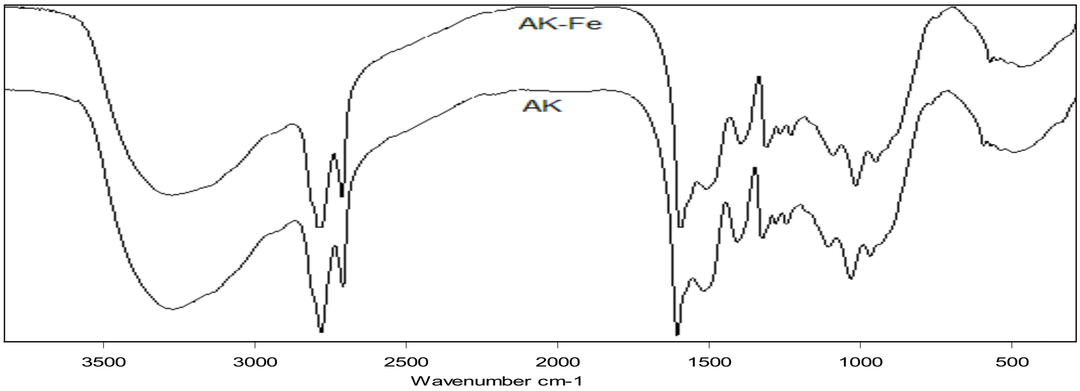

Figure 3(b): FT-IR spectra of AK, AK-Fe adsorbents

3.1.2. SEM

The morphology of each adsorbent before and after modification process was illustrated by SEM, Fig. 4 (a-d).

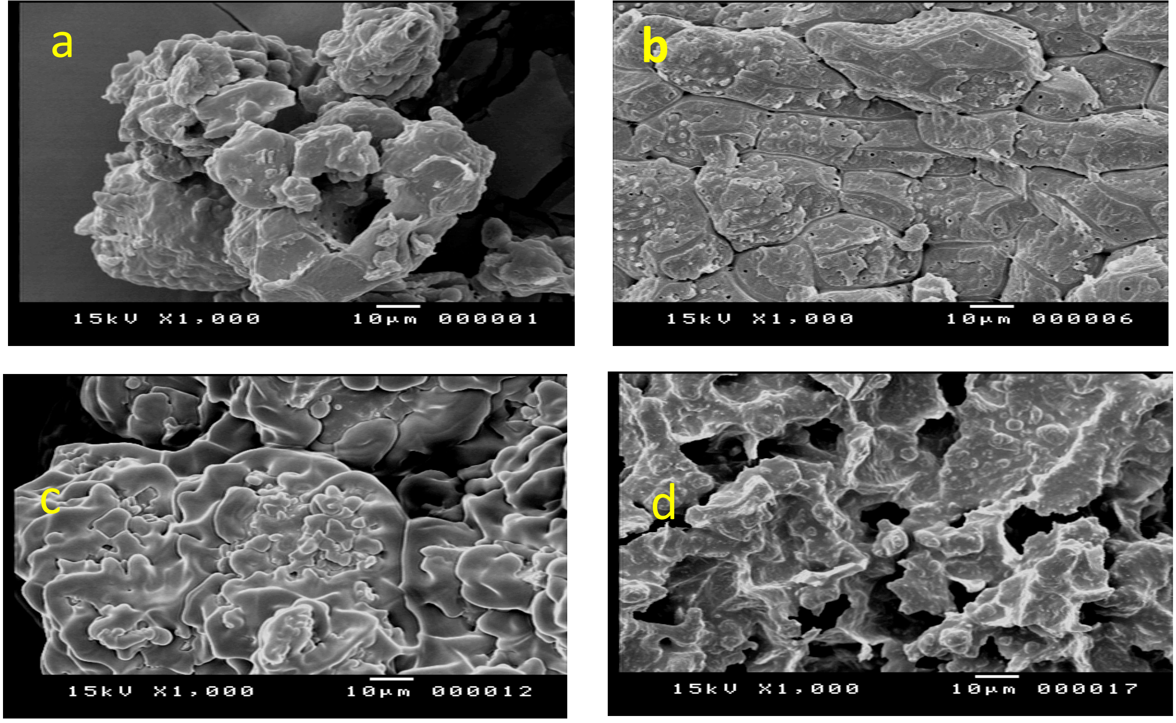

Figure 4: SEM photographs of (a) AHS, (b) AHS-Fe, (c) AK and (d) AK-Fe adsorbents

The SEM photograph of AHS shows that the particles of this adsorbent are gathered with each other as one block. After modification (AHS-Fe), the particles are bounded and rearranged with porous surface due to binding with Fe(III). On the other hand, in the case of AK (Fig. 4 c) its shape was changed due to modification in AK-Fe as it becomes more porous.

3.2. Effect of pH on dye adsorption

The point of zero charges for AHS, AHS-Fe, AK, and AK-Fe adsorbents were found to be 6.2, 6.0, 4.8 and 6.0, respectively using standard potentiometric methods as illustrated in Fig. 5. Therefore, the surface charges of the four adsorbents were positively charged at pH ≤ 6.0. It seems that at pH 1.0–5.0, most of –OH groups are protonated, which are favorable for the adsorption of anionic dyes. However, at high pH, the number of protonated –OH groups will decrease and more –OH ions will be available to compete with the purpurin dye, therefore the adsorption capacity for that dye decreases at high pH. The maximum adsorption capacity for purpurin on all adsorbents was observed at pH 4.0, Fig. 6. The pH of less than 4.0 was not suitable for the adsorption process because the binding site of purpurin was possibly protonated [25]. It was found that the adsorption percent values of AHS and AK were 20.28 and 10.0 %, respectively which lower than those of AHS-Fe and AK-Fe (97.82 and 98.0 %, respectively). This high extraction values can be attributed to the impregnation process which improve the surface area for the two adsorbents (AHS-Fe and AK-Fe) for uptake of purpurin.

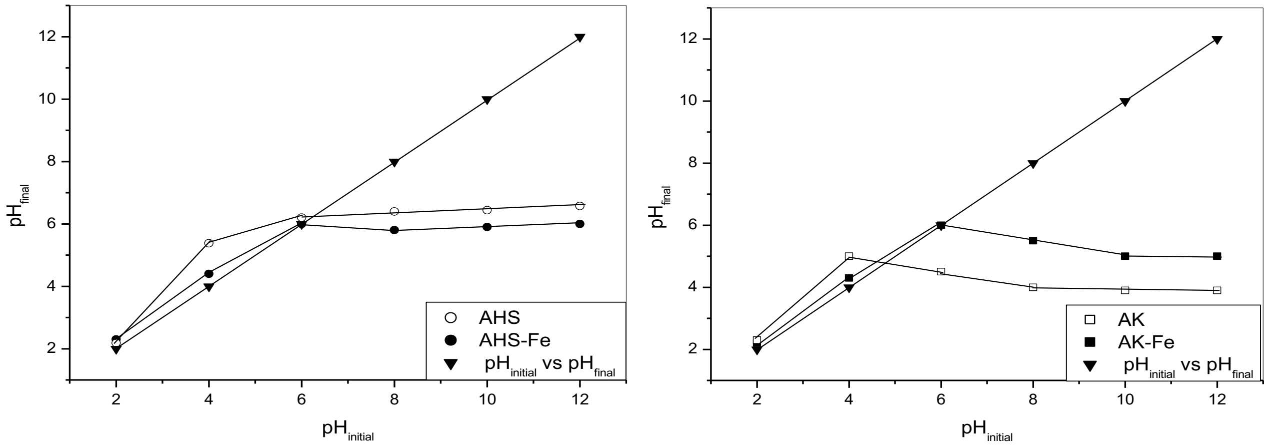

Figure 5: Plot for determination of point zero charge of AHS, AHS-Fe, AK and AK-Fe adsorbents

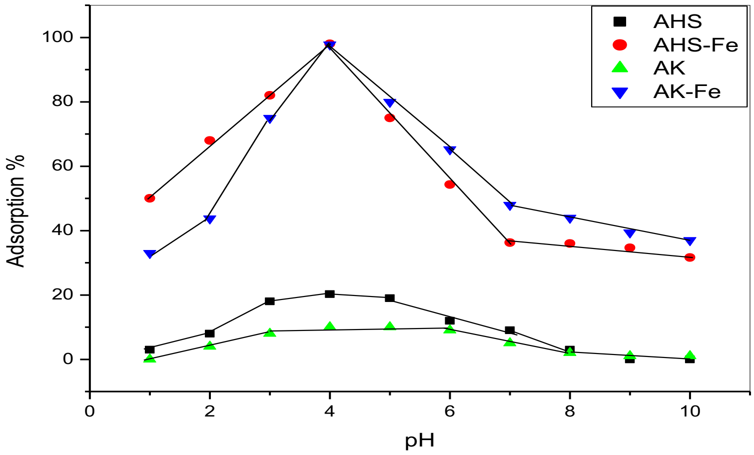

Figure 6: Effect of pH on adsorption percent of AHS, AHS-Fe, AK and AK-Fe adsorbents

Firstly, binary complex was formed between hydroxyl groups on both the adsorbent surface with Fe(III) due to impregnation process. After adsorption of purpurin dye, a ternary complex was formed between Fe(III) and hydroxyl groups in that dye [26], Fig. 7. At pH above 4.0, the adsorption capacity for the all phases decreased gradually. The decrease in adsorption capacity at high pH values is attributed to the accumulation of a negative charge at the adsorbent surface, providing relatively fewer effective sites for dye adsorption due to an increase in repulsive forces [27]. Thus, it was concluded that the lowest possible pH should be maintained for efficient adsorption of purpurin from aqueous solutions.

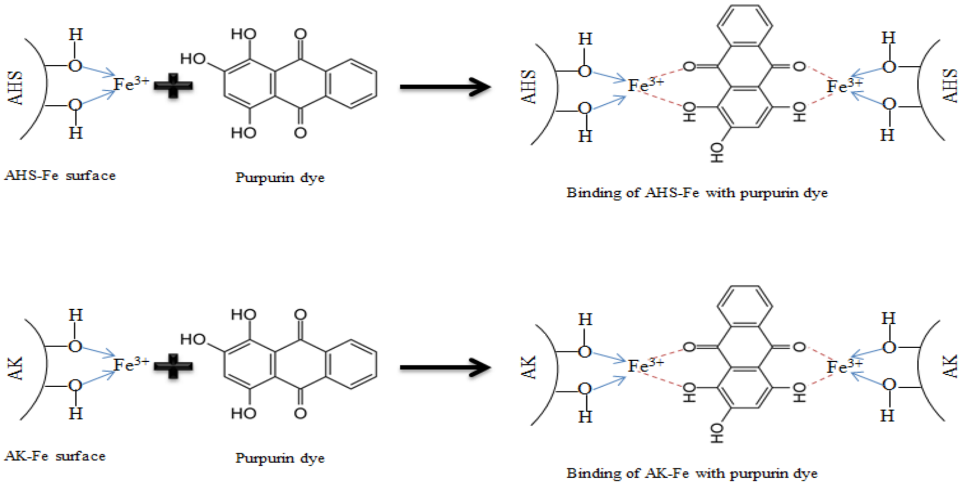

Figure 7: Suggested mechanisms of the complex formation between both AHS-Fe and AK-Fe with purpurin dye

3.3. Effect of adsorbent dosage

The weight of each adsorbent was varied from 10.0 to 100.0 mg keeping all the other experimental variables, viz., pH 4.0 initial concentrations (10^{-4}) and contact time 30 min. Fig. 8 represents the adsorption percentage versus the adsorbent dosage (mg). It may be observed that on increasing the adsorbent weight, the adsorption percentage increased up to a weight of 50.0, 50.0, 20.0 and 30.0 mg for AHS, AK, AHS-Fe and AK-Fe, respectively then remained constant.

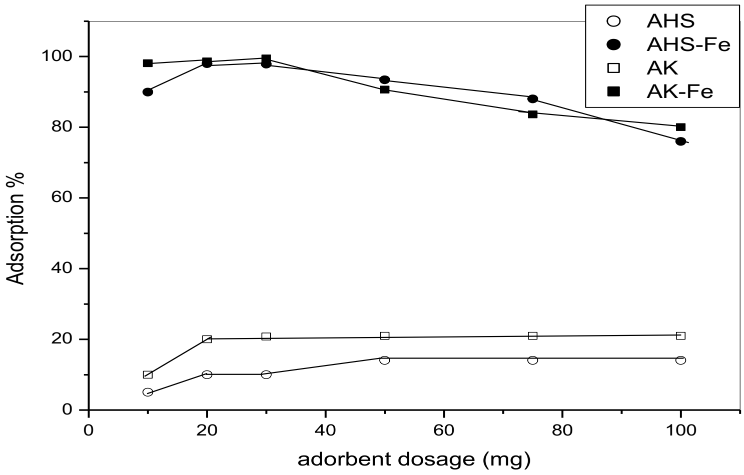

Figure 8: Effect of adsorbent amount on adsorption percent of AHS, AHS-Fe, AK and AK-Fe adsorbents

3.4. Effect of shaking time

Shaking time is an important factor in the process of evaluation of the adsorbent. The batch experiments were carried out at different contact times 5, 15, 20, 30 and 45 min using mechanical shaker. Results of adsorption percentage of purpurin as a function of shaking time intervals are represented in Fig. 9. The equilibrium is reached within the first 30 min of contact and reached a saturation level. In the beginning, the purpurin dye adsorbed, occupied selectively the active sites on each phase. As the contact time increased the active sites on the adsorbent were filled. The results clearly indicate that the equilibrium for purpurin dye is attained in 30 min of contact.

3.5. Effect of dye concentration

The effects of initial dye concentrations on the rate of adsorption by AHS, AHS-Fe, AK and AK-Fe are explored in the range from 1.0×10^{-4} to 3.0×10^{-4} mol/L of purpurin dye (Fig. 10). It is evident from the figure that the amount dye adsorbed increases from 6.4 to 17.94 mg/g for AHS, from 8.97 to 18.83 mg/g for AK, from 84.55 to 126.37 mg/g for AHS-Fe and from 70.37 to 88.46 mg/g for AK-Fe, respectively. It is obvious that the removal of the dye by various adsorbents were dependent on the concentration of the dye since the increase in the initial dye concentration increased the amount of the dye adsorbed on the adsorbents. Moreover, the initial rate of adsorption was greater for higher initial dye concentration because the resistance to the dye uptake decreased as the mass transfer driving force increased.

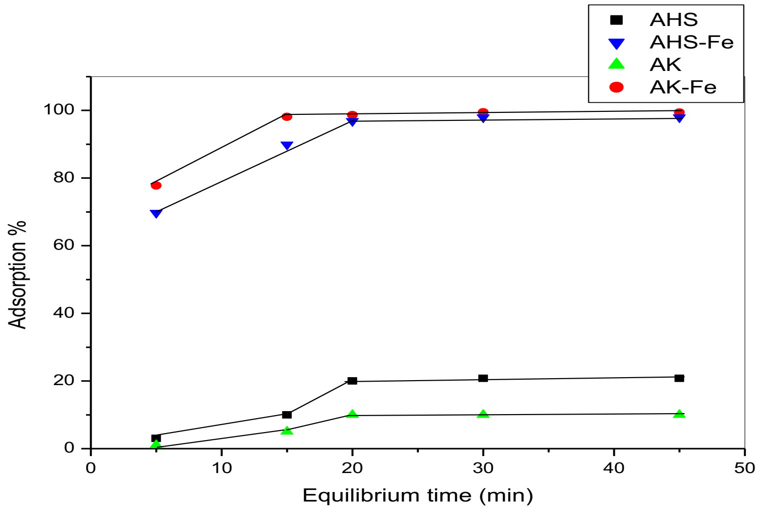

Figure 9: Effect ofequilibrium time on adsorption percent of AHS, AHS-Fe, AK and AK-Fe adsorbents

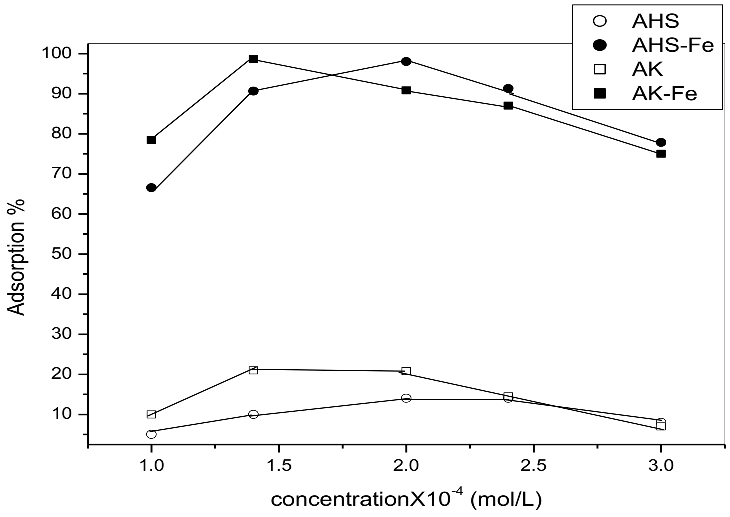

Figure 10: Effect ofconcentration of purpurin dye on adsorption percent of AHS, AHS-Fe, AK and AK-Fe adsorbents.

3.6. Application to environmental samples

The applicability and usefulness of the developed methodology were tested for removal of purpurin dye via these two novel adsorbents (AHS-Fe and AK-Fe) in different environmental water samples. The recovery was examined by spiking a known volume of dye and results are presented in Table 1.

Table 1: Results obtained for purpurin dye determination in various water samples after adsorption by AHS-Fe and AK-Fe adsorbents

Adsorbent	Water sample	Spiked purpurin dye (10^{-4} mol L^{-1})	Mass of the phase (mg)	Recovery^{a} (%)
AHS-Fe	GW	2.0	20.0	98.00 ± 0.1
AK-Fe		1.4	30.0	98.56 ± 0.05
AHS-Fe	NRW	2.0	20.0	98.3 ± 0.05
AK-Fe		1.4	30.0	98.97 ± 0.01
AHS-Fe	DTW	2.0	20.0	97.99 ± 0.5
AK-Fe		1.4	30.0	98.45 ± 0.1
AHS-Fe	SW	2.0	20.0	97.97 ± 0.03
AK-Fe		1.4	30.0	98.8 ± 0.01

* Average of three determinations

The high recoveries of spiked samples obtained by this method indicate the capability for the determination of the understudied dye. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Conclusion

A simple and new solid-phase extraction procedure, based on impregnation of AHS and AK with Fe(III) has been developed. The adsorption capacity values of prepared AHS-Fe and AK-Fe were investigated by batch experiments and equal 126.37 and 88.46 mg/g, respectively. This revealed that these two new adsorbents were effectively removing of purpurin dye. Also, the proposed method has been applied to determine purpurin in environmental samples with high recovery values and no matrix interference.

Acknowledgments-The authors are pleased to acknowledge Faculty of science in Minia University for providing the facilities for the research.

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