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

J. Mater. Environ. Sci., 2020, Volume 11, Issue 10, Page 1699-1709

http://www.jmaterenvironsci.com

Copyright © 2020,
University of Mohammed Premier
Oujda Morocco

Impregnation and characterization of Eco - friendly adsorbent for removal of an azo dye from water samples

Asmaa M. Abdel Rahim[a*]

[a]*Department of Chemistry, College of Science, University of Hafr Al Batin, P.O. Box 1803, Hafr Al Batin, 31991, Saudi Arabia*

Received 22 July 2020,
Revised 11 Sept 2020,
Accepted 12 Sept 2020

Keywords
- ✓ *Fe@MSWEn,*
- ✓ Impregnation,
- ✓ Calmagite dye,
- ✓ Mango seed woody endocarp,
- ✓ Water samples.

amoheyeldin@uhb.edu.sa ;
Phone: +966532543816;
Fax: 0137203426

Abstract

In this work, preparation of environment friendly adsorbent based on impregnation of mango seed woody endocarp (MSWEn) with Fe(III) (Fe@MSWEn) as low-value agricultural by-product is reported for removal of Calmagite dye (azo dye) from water samples. To emphasis the success of this modification method, the prepared adsorbent was characterized by FT-IR, SEM and X-ray diffraction. Different adsorption factors such as pH, contact time and weight of adsorbent were studied to investigate adsorption of Calmagite dye on Fe@MSWEn. The adsorption percent and the adsorption capacity of Calmagite using this adsorbent at pH = 2.0 were found to be 97.97 % and 2106.57 μg g^{-1}, respectively. Regeneration of adsorbent was easily performed by adsorption/desorption experiments followed for 2 cycles. Finally, the new adsorbent was used successfully for the removal of Calmagite dye from different water samples with high recoveries.

1. Introduction

Dyes are among the most important resources of water pollution. Synthetic azo-dyes such as calmagite are widely used in various industries like textile, cosmetic, paper, food, paint, printing and pharmaceutical [1]. Their effluent is hard to treat because of the complex aromatic structure of dyes, which make them more stable and difficult to biodegrade. They also exhibit toxic and carcinogenic effects toward biological systems [2, 3]. Different techniques like electrochemical degradation, ozonation, oxidation, photocatalysis, membrane filtration, adsorption, and biological treatment have been employed in removal of dye [4, 5]. But none of these methods were successful in completely removing the color from wastewater. Among these methods adsorption is shown to be potentially powerful method for removal of dye due to its efficiency [6]. Dyes can be effectively removed by adsorption process; in which dissolved dye compounds attach themselves to the surface of adsorbents. Most of the adsorption studies have been focused on environment friendly waste materials used as adsorbents for removal of dyes from water such as apricot stone [7], banana peel [8, 9], lemon peel [10], nut shell [11] and sugar cane bagasse ash [12]. Mango seed endocarp is one of promised adsorbents for removal of dye due to its structure which rich in functional groups have the ability to remove dye from water. These functional groups are hemicelluloses, cellulose and lignin which also are favorable for binding with metal ions such as Fe(III).

On the other hand, the use of these waste materials as adsorbents requires some procedures to increase their removal ability. These procedures include the process of modification which performing by the addition of some material to its surface. Most of these procedures are complicated and take several steps [13 - 15], so it was necessary to search for a simple, time saving, low cost and effortless method. For this reason, impregnation process was used for increasing the selectivity and loading capacity of adsorbent surface by adding metal ions with a simple procedure [2, 16 - 18].

In the best of our knowledge, there is no studies for impregnation of MSWEn with Fe(III). So, this paper aims to preparation of low cost and environment friendly adsorbent using simple modification process. MSWEn was impregnated with Fe(III) to develop an efficient adsorbent (Fe@MSWEn) for removal of Calmagite dye from water sample.

2. Materials and methods

2.1. Chemicals

Fresh mangoes were obtained from a local market in Minia, Egypt. Doubly distilled water (DDW) was used throughout all experiments. Ferric chloride ($FeCl_3.6H_2O$) and Calmagite dye were analytical grade from Merck, Germany. ACS reagent grade hydrochloric acid and sodium hydroxide were obtained from Aldrich. Samples of Nile River water (NRW), drinking tap-water (DTW) and ground water (GW) were collected from Minia. Also, sample of waste water (WW) was taken near the drainage of the sugar plant in Minia, Egypt.

2.2. Impregnation of Mango seed endocarp

2.2.1. Preparation of mango seed endocarp

The seeds (three samples) were removed manually using stainless steel knives and opened to get endocarps. These endocarps were cut into pieces then were washed with DDW and air dried. The dried material was ground in a mill and sieved to obtain small particles. These small particles were washed with DDW and dried well in room temperature. Then, it was kept in a closed dark glass bottles and stored until utilization [2].

2.2.2. Preparation of impregnated adsorbent with Fe(III)

500.0 mg of MSWEn was soaked for two days in 50.0 mL of 0.5 M $FeCl_3.6H_2O$ solution (its pH was adjusted to 3.5 by adding drops of 1.0 M NaOH and 1.0 M HCl) for 24 hrs. Then this mixture was filtrated and washed with DDW in order to remove the residues of $FeCl_3$ as the filtrate being colorless. The obtained adsorbent was left to dry at room temperature. The color of MSWEn was converted from beige color into dark grey color which confirmed the success of the impregnation process, Fig. 1. Moreover characterization of Fe@MSWEn also supports the modification process via impregnation method.

2.3. Characterization of mango seed endocarp

Fourier transform infrared (FT-IR) spectroscopy (410 JASCO, Japan) was used for analyze the surface functional groups of MSWEn and Fe@MSWEn adsorbents. The surface morphology of the two adsorbents were characterized using scanning electron microscopy (JSM-5400 LV JEOL, Japan). The crystal structure of the adsorbents was studied using X-ray diffractometer (JSX-60 PA JEOL, Japan).

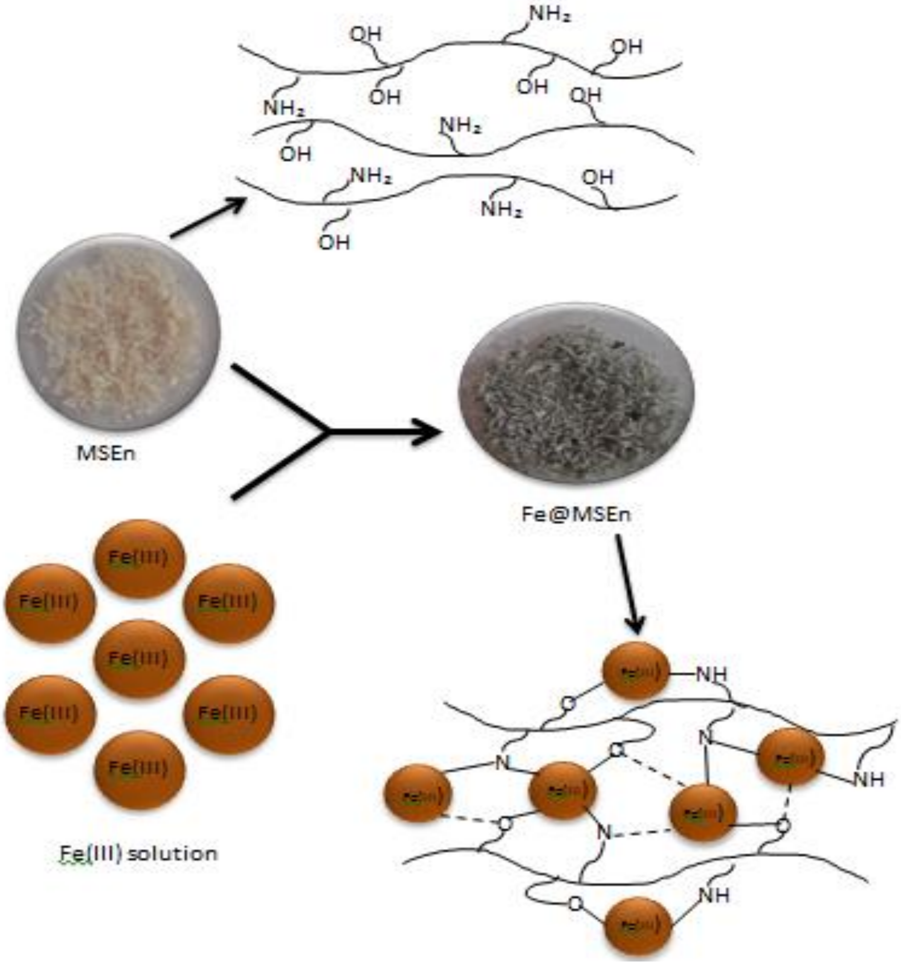


Figure 1: Impregnation of MSWEn with Fe(III)

2.4. Studies on point zero charge (pH_{zpc}) of adsorbent

In pH_{zpc} determination, 200.0 mg of each adsorbent (MSWEn and Fe@MSWEn) was added to 50.0 mL of 0.01 M NaCl and its pH was adjusted in the range of 2.0 – 12.0 by adding appropriate volumes of 1.0 M HCl or 1.0 M NaOH [19]. These flasks were kept for 48 hrs 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 $pH_{initial}$.

2.5. Batch adsorption experiments

The adsorption experiments were carried out using batch method. Different parameters such as, effect of pH, adsorbent amount and contact time were studied. Definite weight of each adsorbent (MSWEn and Fe@MSWEn) was added to 50.0 mL of 1.0×10^{-4} M of Calmagite dye. Different additions of 1.0 M NaOH or 1.0 M HCl solutions were used for justifying the pH values before adding the adsorbent. The solution was then shaken by Wrist Action mechanical shaker model 75 (manufactured by Burrell Corporation Pittsburgh. PA. U.S.A.) 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 (Perkin Elmer Lambda 35 UV/Visible spectrophotometer, England) by recording the absorbance changes at a wavelength of maximum absorbance (602 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.

2.6. Removal of calmagite dye from environmental water samples

Different water samples drawn from Nile River water (NRW), drinking tap-water (DTW), waste water (WW) 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. 50.0 mg of Fe@MSWEn was conditioned with 50.0 mL of each water sample spiked with 3.0 mL of 1×10^{-4} mol/L of Calmagite dye after adjusting the pH of samples to the optimum pH value 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. Results and discussion

3.1. Characterization of adsorbent

3.1.1. FT-IR

The main characteristic functional groups for both MSWEn and Fe@MSWEn adsorbents were analyzed using FT-IR spectra, Fig. 2. In MSWEn spectrum, the broad overlapping band at 3421 cm^{-1} can be attributed to υ(O–H) groups contained in lignin, cellulose and hemicelluloses. The band observed at 2921 cm^{-1} is assigned to asymmetric C–H band. The two strong absorption peaks at 1737 and 1624 cm^{-1} were assigned to carbonyl C=O stretching (present in esters, aldehydes, ketones groups and acetyl derivatives) and C=C, respectively [20]. These all bands changes after impregnation process with Fe(III).

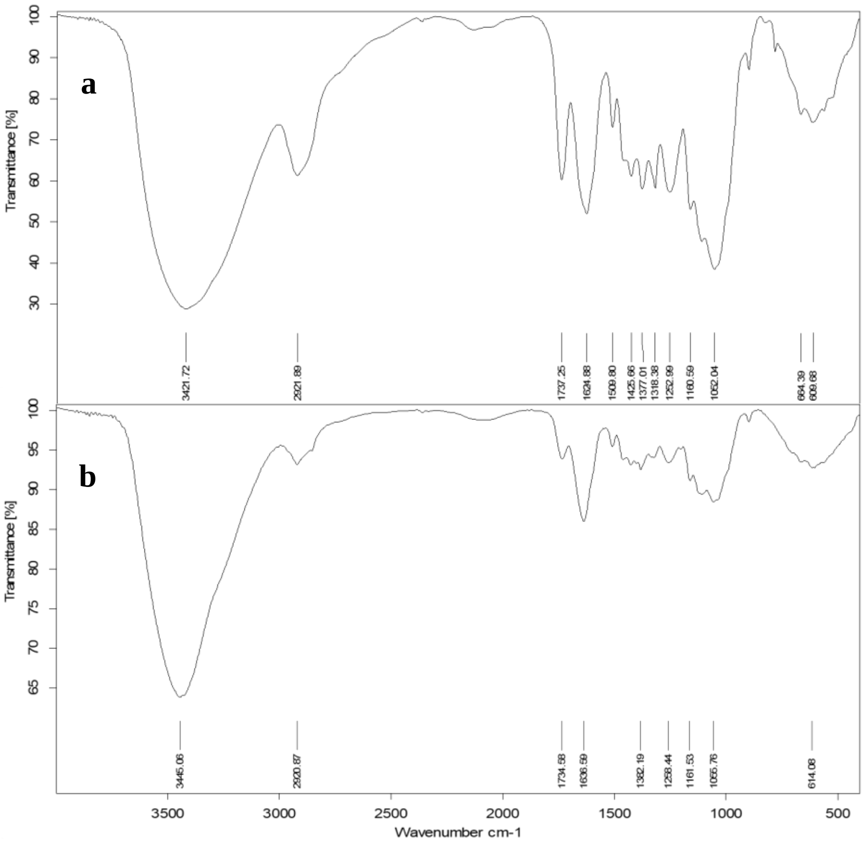


Figure 2: FT-IR spectra of (a) MSWEn and (b) Fe@MSWEn adsorbents

As shown in Fig. 2b, the FT-IR spectrum of Fe@MSWEn adsorbent, the band attributed to υ(O–H) groups increased in the intensity and shifted to 3445 cm^{-1} indicates to the coordination of Fe(III) with hydroxyl groups, Scheme 1(b). Moreover, the band assigned to asymmetric C–H band, decreased in the intensity. The two peaks assigned to carbonyl C=O stretching decreased and shifted to 1734 and 1636 cm^{-1}, respectively. The changes intensity and shifts in the transmittance bands in the FTIR spectrum were directly related to the impregnation of MSWEn adsorbent with Fe(III). In addition, an obvious color changes from flesh of MSWEn to black of Fe@MSWEn which confirm the success of modification process via impregnation procedure.

3.2. X-ray

The X-ray diffraction spectra of the MSWEn and Fe@MSWEn adsorbents were shown in Fig. 3. MSWEn adsorbent showed a broad hump which indicates that the surface of MSWEn is amorphous. After impregnation of MSWEn with Fe(III), the bands of MSWEn was decreased in intensity and the peak of Fe(III) was appeared close to the band of MSWEn. These changes of the structure of adsorbent confirm the modification on the surface of MSWEn.

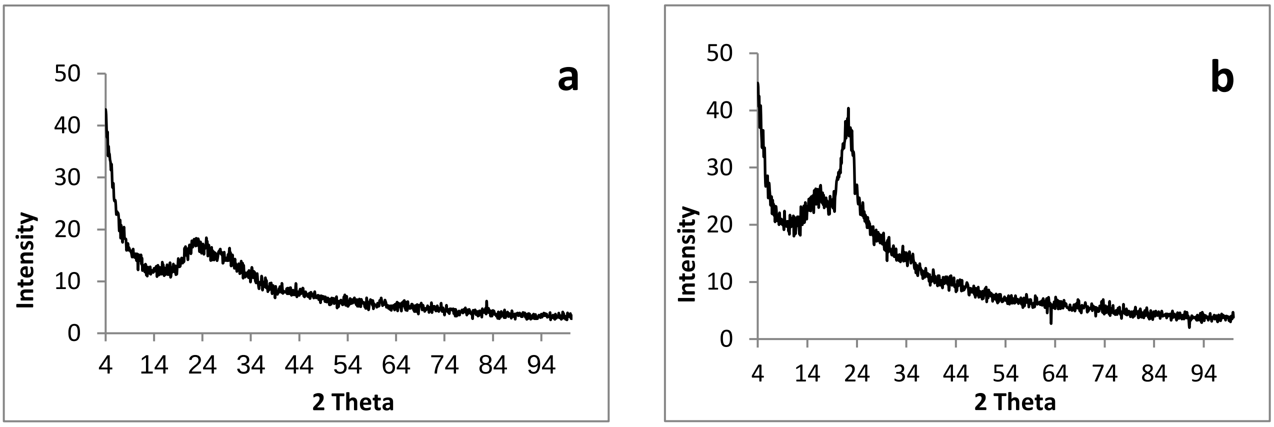


Figure 3: X-ray diffraction patterns of (a) MSWEn and (b) Fe@MSWEn adsorbents

3.1.3. SEM

The microscopic features of the MSWEn and Fe@MSWEn were observed with SEM (Fig. 4). In this figure we can see the morphology of MSWEn as it seems to be rough surface. After impregnation process of MSWEn with Fe(III), the particles of Fe@MSWEn showed to be gathered and converts into smooth surface. This confirm that Fe(III) was strongly binding with the surface functional groups on MSWEn which rich in hydroxyl groups.

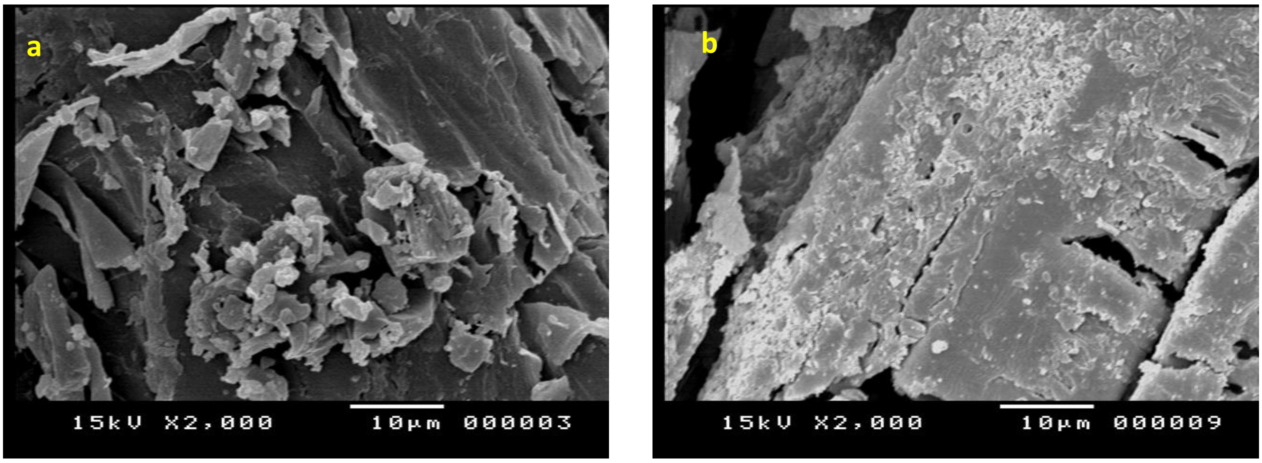


Figure 4: SEM micrographs of (a) MSWEn and (b) Fe@MSWEn adsorbents

3.2. Effect of pH on dye adsorption

The form of analyte in aqueous solution and the surface charge of adsorbent can be determine by study the effect of pH of sample solution which plays an important role in the adsorption process [21]. By determine the pH_{zpc} for each of investigated adsorbent, it was found that the surface charges of MSWEn and Fe@MSWEn was 3 and 4.5, respectively using standard potentiometric method, Fig. 5.

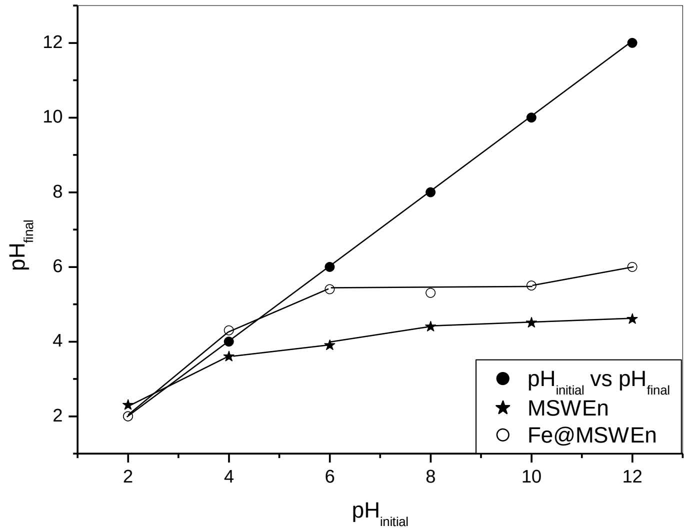


Figure 5: Plot for determination of point zero charge of MSWEn and Fe@MSWEn adsorbents

To evaluate the effect of sample pH on the adsorption of Calmagite dye, the pH of the solution varied in the range of 1.0 –10.0. As shown in Fig. 6, the two adsorbents showed the maximum uptake for Calmagite dye at pH = 2.0. It was found that, the MSE-Fe adsorbent has higher adsorption percent and capacity (97.97 % and 2106.57 µg g^{-1}) than MSWEn adsorbent (47.74 % and 1026.51 µg g^{-1}). This can be explained by the two following suggested mechanisms: in the case of MSWEn adsorbent, below the pH_{zpc} at pH = 2.0, the surface charge of this adsorbent is positive where the hydroxyl groups of the MSWEn−OH became protonated as follow:

$$\text{MSWEn−OH} + H^+ \leftrightarrow \text{MSWEn} -OH_2^+$$

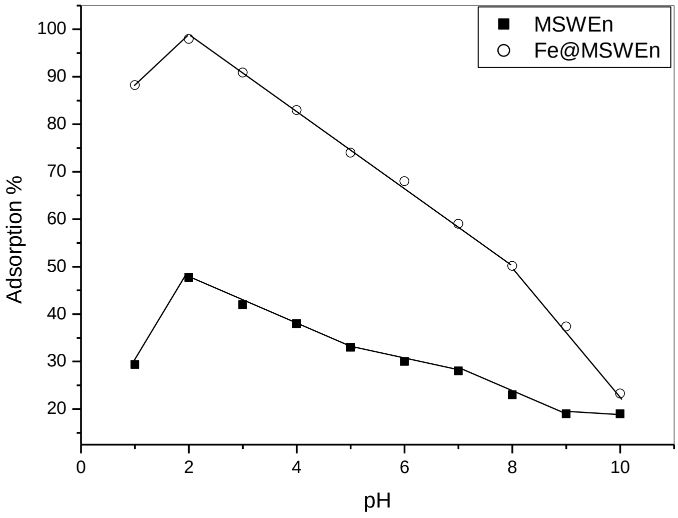


Figure 6: Effect of pH on adsorption percent values of MSWEn and Fe@MSWEn adsorbents

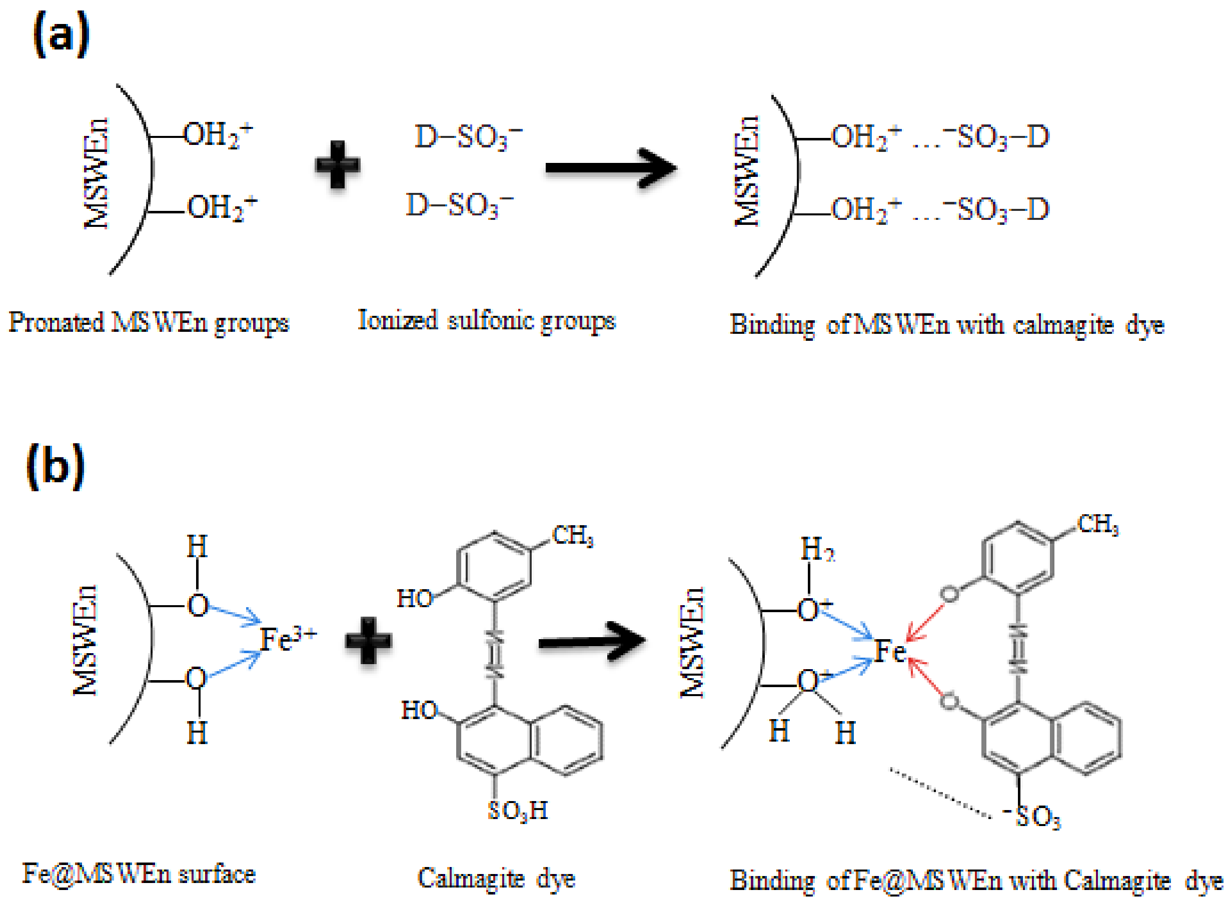
Also, the Calmagite dye was dissolved and converted to anionic dye ions having negatively charged sulfonic groups $D{-}SO_3^-$.

$$D{-}SO_3H \rightarrow D{-}SO_3^- + H^+$$

Then, the adsorption process progressing due to the electrostatic attraction between the two oppositely charged ions, Scheme 1(a).

On the other hand, for Fe@MSWEn adsorbent, the highest adsorption percent can be attributed to the complex formation and the electrostatic interactions as showed in Scheme 1(b).

By increasing the pH of the solution beyond the pH_{zpc}, the surface charge of adsorbent becomes negative where more OH^- ions will be available to compete with the anionic sulfonic group in Calmagite dye. Therefore, the two adsorbents displayed a sharp decrease in the uptake values.



Scheme 1: Suggested mechanisms of: (a) the ionic interaction between MSE and Calmagite dye, (b) the ternary complex formation and ionic interaction between Fe@MSWEn and Calmagite dye

3.3. Effect of adsorbent amount

The weights of the two adsorbents were varied from 10.0 to 100.0 mg keeping all the other experimental variables constant. The results in Fig. 7 showed that, the adsorption percent of Calmagite dye not affected by increasing the weight of MSWEn up to 100.0 mg with adsorption capacity of 1026.51 µg g^{-1}. But in the case of Fe@MSWEn, the adsorption percent increased with increasing the amounts of adsorbent up to 50.0 mg where adsorption capacity values ranged from up 820.5 to and 2106.57 µg g^{-1}. It was shown that the impregnation process carried out increased the Fe@MSWEn capacity for adsorption of analyte. Furthermore, more than 50.0 mg of Fe@MSWEn, the adsorption percent decreased.

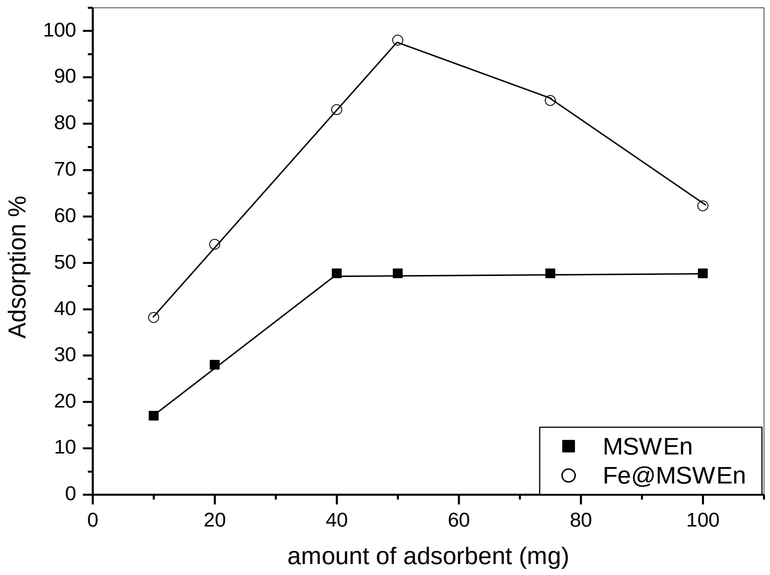


Figure 7: Effect of adsorbent amount on adsorption percent of MSWEn and Fe@MSWEn adsorbents

3.4. Effect of equilibrium time

Adsorption percent values were determined using the batch method at different shaking times (5, 10, 15, 25, 30 and 60 min) to determine the time needed to attain equilibrium using the MSWEn and Fe@MSWEn adsorbents. The adsorption percent for Calmagite dye at the optimum pH value was calculated at each time interval relative to highest uptake at 30 min for both the two adsorbents, Fig. 8. It was found that, the adsorption percent of Calmagite dye on 50.0 mg Fe@MSWEn equals 97.97 % but on 100.0 mg MSWEn equals 67.84 % at 30 min.

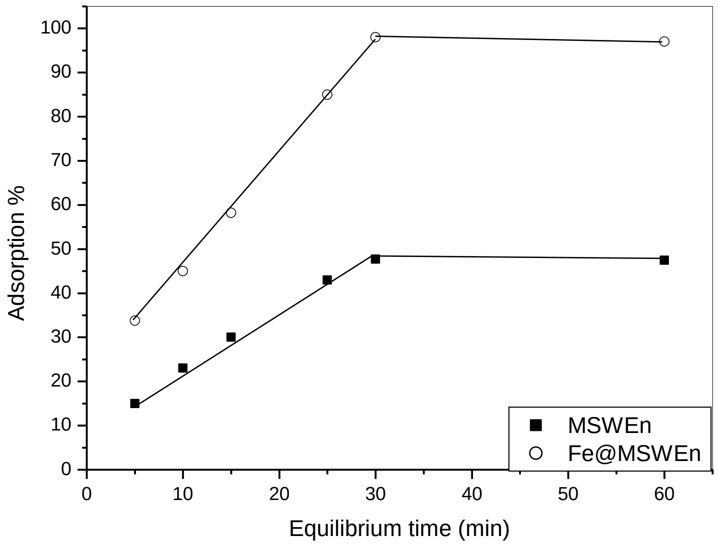


Figure 8: Effect of equilibrium time on adsorption percent of MSWEn and Fe@MSWEn adsorbents

With this data, it was decided that Fe@MSWEn is the best adsorbent for extraction and removal of Calmagite dye.

3.5. Desorption and regeneration studies

Studies of desorption is important in order to regenerate the phase and recover the analyte [22]. Desorption experiments have been performed for Fe@MSWEn adsorbent in acidic ethanol at pH range from 1.0 to 6.0. The results in (Fig. 9) show that the maximum desorption efficiency was 100.0 % ± 0.1

with acidic ethanol at pH = 6.0. The adsorption percentage remained steady at about 97.97 % in the first two cycles, and then the removal efficiency of Calmagite dye decreased.

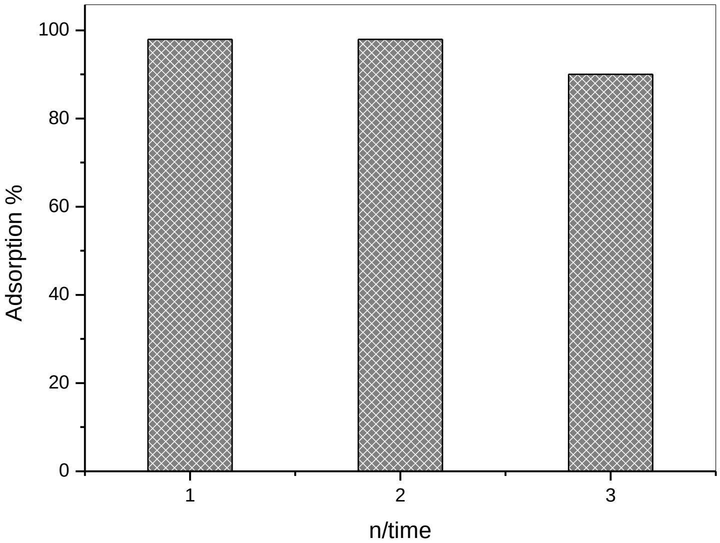


Figure 9: Effect of recycled Fe@MSWEn adsorbent on Calmagite dye adsorption percent

3.6. Removal of Calmagite dye from real water samples

Removal of dissolved dyes from different real water samples by sorption processes, as one of the most effective processes, is always planned and aimed. Therefore, the following section is devoted toward extraction and removal of Calmagite dye from real water samples GW, NRW, DTW and WW using Fe@MSWEn. As illustrated in Table 1, the recoveries for on Fe@MSWEn adsorbent were 97.56, 97.9, 98.8 and 98.0 %, respectively for each water sample. These recovery values indicate the suitability and validity of using Fe@MSWEn adsorbent for removal of Calmagite dye.

Table 1: Results obtained for Calmagite dye determination in various water samples after adsorption by Fe@MSWEn adsorbent

Water sample	Spiked Calmagite dye (10^{-4} mol L^{-1})	Mass of the phase (mg)	Recovery[a] (%)
GW	3.0	50.0	97.56 ± 0.05
NRW	3.0	50.0	97.9 ± 0.1
DTW	3.0	50.0	98.8 ± 0.01
WW	3.0	50.0	98.0 ± 0.1

[a] average of three determination

Conclusion

Impregnation process was used for developing of a new adsorbent from agriculture waste material for removal of Calmagite dye from water samples. Mango seed woody endocarp was impregnated with Fe(III) for removal of investigated dye. Characterization of MSWEn before and after impregnation process using different tools of analysis such as FT-IR, XRD and SEM confirm the success of the modification process of MSWEn. Moreover, all batch adsorption experiment parameters showed that Fe@MSWEn has the high efficiency and adsorption percent for removal of Calmagite dye from different water samples. This adsorbent is promised for using for Calmagite dye removal.

References

1. M. B.Gholivand, Y. Yamini, M. Dayeni, S. Seidi, E. Tahmasebi, Adsorptive removal of alizarin red-S and alizarin yellow GG from aqueous solutions using polypyrrole-coated magnetic nanoparticles, *Journal of Environmental Chemical Engineering,* 3 (2015) 529-540.
2. S.A. Ahmed, A.A.A Gaber, A.M.A. Rahim, Removal of calmagite dye from aqueous media using nanoparticles of mango seed kernel–impregnated Fe (III), *International Journal of Advanced Research*, 3 (2015) 621-632.
3. F.A. Ugbe, N. Abdus-Salam, Kinetics and thermodynamic modelling of natural and synthetic goethite for dyes scavenging from aqueous systems, *Arabian Journal of Chemical and Environmental Research*, 7(1) (2020) 12–28.
4. C. K. Araújo, G.R. Oliveira, N.S. Fernandes, C.L. Zanta, S.S.L. Castro, D.R. da Silva, C.A. Martínez-Huitle, Electrochemical removal of synthetic textile dyes from aqueous solutions using Ti/Pt anode: role of dye structure. *Environmental Science and Pollution Research,* 21 (2014) 9777-9784.
5. H. Wang, X. Yuan, G. Zeng, L. Leng, X. Peng, K. Liao, Z. Xiao, Removal of malachite green dye from wastewater by different organic acid-modified natural adsorbent: kinetics, equilibriums, mechanisms, practical application, and disposal of dye-loaded adsorbent. *Environmental Science and Pollution Research,* 21 (2014) 11552-11564.
6. W.W. Ngah, M.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, *Bioresource Technology,* 99 (2008) 3935-3948.
7. A.M.A. Rahim, Apricot stone- impregnated Fe(III): an efficient, novel and eco-friendly adsorbent for removal of purpurin dye from environmental water samples, *J. Mater. Environ. Sci.* 9 (2018) 444-451
8. M. Dahiru, Z.U. Zango, M.A. Haruna, Cationic dyes removal using low-cost banana peel biosorbent, *American Journal of Materials Science,* 8 (2018) 32-38.
9. K. Amela, M.A. Hassen, D. Kerroum, Isotherm and kinetics study of biosorption of cationic dye onto banana peel, *Energy Procedia,* 19 (2012) 286-295.
10. A. Bhatnagar, E. Kumar, A.K. Minocha, B.H. Jeon, H. Song, Y.C. Seo, Removal of anionic dyes from water using Citrus limonum (lemon) peel: equilibrium studies and kinetic modeling, *Separation Science and Technology,* 44 (2009) 316-334.
11. P.S. Kumar, S. Ramalingam, K. Sathishkumar, Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent. *Korean Journal of Chemical Engineering,* 28 (2011) 149-155.
12. S.M. Kanawade, R.w. Gaikwad, A. Misal, Low cost Sugarcane Bagasse Ash as anAdsorbent for Dye Removal from Dye Effluent, *International Journal of Chemical Engineering and Applications,* 1 (2010) 309.
13. Y.O. Khaniabadi, M.J. Mohammadi, M. Shegerd, S. Sadeghi, S. Saeedi, H. Basiri, Removal of Congo red dye from aqueous solutions by a low-cost adsorbent: activated carbon prepared from Aloe vera leaves shell, *Environmental Health Engineering and Management Journal*, 4 (2017) 29-35.
14. X. Gao, Y. Dai, Y. Zhang, X. Zhai, F. Fu, Effective Dye Removal from Waste Water Using a Novel Low-Cost NaOH-Modified Fly Ash, *Clays and Clay Minerals,* 64 (2016) 695-705.
15. C.D. Atemkeng , T. Kamgaing , D.R. Tchuifon Tchuifon, G. Doungmo , L.A. Amola, A.T. Kamdem, S.G. Anagho, Chemical preparation and physicochemical characterization of powdered activated carbons based on safou (Dacryodes edulis) seeds, *J. Mater. Environ. Sci*., 11(6) (2020) 896-910.

16. E.M. Soliman, H.M. Albishri, H.M. Marwani, M.G. Batterjee, Removal of 2-chlorophenol from aqueous solutions using activated carbon-impregnated Fe(III), *Desalination and Water Treatment*, 51 (2013) 6655-6662.
17. G. Ghanizadeh, M., Ehrampoush, M. Ghaneian, Application of iron impregnated activated carbon for removal of arsenic from water, *Journal of Environmental Health Science & Engineering*, 7 (2010) 145-156.
18. J.T. Utsev, R.T. Iwar, K.J. Ifyalem, Adsorption of Methylene Blue from Aqueous Solution onto Delonix regia Pod Activated Carbon: Batch Equilibrium Isotherm, Kinetic and Thermodynamic Studies, *J. Mater. Environ. Sci.*, 11(7) (2020) 1058-1078.
19. Y.C. Sharma, V. Srivastava, C.H. Weng, S.N. Upadhyay, Removal of Cr (VI) from wastewater by adsorption on iron nanoparticles, *The Canadian Journal of Chemical Engineering*, 87 (2009) 921-929.
20. I.O. Okeowo, E.O. Balogun, A.J. Ademola, A.O. Alade, T.J. Afolabi, E.O. Dada, A.G. Farombi, Adsorption of Phenol from Wastewater Using Microwave-Assisted Ag–Au Nanoparticle-Modified Mango Seed Shell-Activated Carbon, *International Journal of Environmental Research*, 14 (2020) 215-233. https://doi.org/10.1007/s41742-020-00244-7
21. J. Wang, Z. Chen, Z. Li, Y. Yang, Magnetic nanoparticles based dispersive micro-solid-phase extraction as a novel technique for the determination of estrogens in pork samples, *Food Chemistry*, 204 (2016) 135-140.
22. S.A. Ahmed, A.A.A Gaber, A.M.A. Rahim, Novel solid phase-extractor based on functionalization of silica fume with 8-hydroxyquinoline for determination of Pb(II) in water samples by square-wave adsorptive stripping voltammetry, *European Journal of Materials Science and Engineering* 4(4) (2019) 173-189.

(2020) ; http://www.jmaterenvironsci.com