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COFFEE SPENT SUPPORTED Fe-Al-Zr COMPOSITE: SYNTHESIS, CHARACTERIZATION AND ITS ADSORPTIVE DYE REMOVAL FROM TANNERY WASTEWATER

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ABSTRACT. This work was conducted to evaluate the adsorption performance of coffee spent modified Fe-Al-Zr composite. The $Al_2O_3/Fe_3O_4/ZrO_2$ ternary oxide system was efficiently synthesized from the respective salt precursors by a two-step co-precipitation method under nitrogen atmosphere in basic condition. XRD, SEM-EDX, FTIR and ICP-OES were used to characterize the features of the adsorbents. The pH point of zero charge of the selected adsorbent was also determined. Batch adsorption experiment was conducted under different conditions such as contact time, initial concentration of dye, pH, sorbent dosage and agitation speed. The Langmuir and Freundlich, isotherms were tested to examine the adsorption behavior. The equilibrium data was well fitted to Langmuir isotherm model. The maximum adsorption capacity (q_o) was 8.4 mg/g for acidic brown 75 dyes. The kinetic data correlated ($R^2 = 0.999$) well with the pseudo second order kinetic model. To evaluate the practical applicability of the coffee spent supported nanocomposite adsorbent to real samples, effluent was collected from Batu Leather Industry. The result demonstrated 95.7% (10 mg/L) removal efficiency of the dye by the as-obtained composite indicating its potential application for environmental application.

KEY WORDS: Coffee spent, Nanocomposite, Sorption, Textile dye, Immobilization

INTRODUCTION

There are more than 10,000 commercially available dyes and over $7x10^5$ tones of synthetic dyes being produced annually across the world [1]. Acid dyes are highly water-soluble anionic dyes, due to the presence of sulfonic acid groups or carboxylic acid groups, forming ionic interactions between the protonated functionalities of fibers ($-NH_3^+$) and the negative charge of the dyes. Acidic brown 75 is one among anionic dyes [7]. Most leather industries extensively use acidic dye and a maximum of 70% of the dye is employed for coloring leaving the remaining amount of dye unused. The fate of the later is discharge into water bodies causing diverse effects on the environment and living organisms [2]. The dye containing effluents can be harmful and block light penetration in water system and have a critical effect on photosynthesis. Further, they reduce dissolved oxygen (DO) level and increase the biochemical oxygen demand (BOD) of the receiving water body [3].

Moreover, dye-containing effluent is recalcitrant and difficult to degrade, carcinogenic and render the receiving water unfit for its intended use. Synthetic dyes greatly disturb the marine ecosystem as they go through chemical and biological changes. The presence of dyes create aesthetically undesirable condition, result in reduced water re-oxygenation capacity, and difficulties in water treatment by biological methods, furthermore preventing the reuse of the water in other process steps [4-5]. Wastewaters dyes are also hardly refined because dye molecules are resistant to aerobic digestion [6].

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The conventional treatment method is not economically feasible and effective for the treatment of dye containing effluents because of the recalcitrant nature of dye molecules. The other treatment technique applied for treatment of dye-contaminated wastewater in tanneries are membrane filtration, electro-chemical methods, reverse osmosis, ion exchange and advanced oxidation processes [8-9]; not economically feasible because of their relatively high investment and operational cost [10].

Wastewater-containing dyes are being treated using adsorption method. It is a simple operation and low-cost method for removal of dyes containing wastewater [11] as compared to physical treatment, chemical precipitation and biological treatment methods [12]. In addition, adsorption has high treatment efficiency and adsorbents can be regenerated for multiple reuses [2].

Nano-composites are materials which are prepared by combining two or more pure substances with particularly distinctive mechanical, electrical, magnetic, optical, thermal, or chemical properties to form a composite material that combines the desirable properties of each other to make a multi-functional substance. Considering the enormous requests for cost-effective and consistent eco-remediation applications, the goal of the present work is to synthesize cost-effective and functionally efficient magnetic composite adsorbent for the effective adsorption of dye by simple separation from wastewater. This would ensure good reusability of adsorbents without altering its adsorption capacity in a relatively short time [13].

Composites with remarkable adsorption capabilities are highly preferred for efficient wastewater remediation. Unfortunately, most of the nanomaterial based adsorbents show inherent limitations such as leaching and agglomeration apart from the recoverability problem due to their small size [13]. Immobilizing nanomaterials onto a bio-support such as coffee spent is one among the various strategies to overcome these challenges [14]. The purpose of this study was, therefore, to evaluate the adsorption performance of coffee spent modified Fe-Al-Zr composite considering acidic brown 75 dyes as a model pollutant. We have also assessed the efficiency of this composite for real sample collected from one of the local tannery located in Addis Ababa City, Ethiopia. Our findings suggest the potential application of this composite sorbent for dye removal from polluted environment.

EXPERIMENTAL

Preparation of adsorbent material

The coffee spent used in this study was collected from the cafeterias at Addis Ababa University, Natural and Computational Science College. The collected sample was washed with distilled water several times to remove any adhering dirt materials and kept in hot air oven at 105 °C for 24 h. Then, the powder was sieved with < 250 μm to get uniform particle size of the sample. The synthesis of coffee spent modified ternary composite was done in three steps.

Synthesis of adsorbent

The magnetic $Al_2O_3/Fe_3O_4/ZrO_2$ metal oxide nanocomposite was prepared in the mole ratios of the metals 25:70:5 by chemical co-precipitation method as reported by Blaney and Lee with some modification [15]. The stock solution containing 1:2 molar ratios (ferrous chloride to ferric chloride) was stoichiometrically calculated and then dissolved into 100 mL of 0.3 M HCl. The obtained iron solution was added drop by drop into the reaction flask containing 120 mL of 3 M NaOH solution. The pH of the mixture was adjusted at 12 using 0.1 M of NaOH and 0.01 M of HCl solution. The solution mixture was vigorously stirred at 80 °C for 2 h under inert atmosphere via nitrogen atmosphere. The reaction mixture was then allowed to cool at room temperature without interruption for 4 h. The product was washed with ultrapure water several times until the filtrate show no formation of white turbidity upon addition of $AgNO_3$ solution. Finally, a suspension of Fe_3O_4 (ferro-fluid) was dried and kept in hot air oven at 105 °C for 24 h. The solution of $Al(NO_3)_3.9H_2O$ and $ZrOCl_2.8H_2O$ (obtained by dissolving 0.465 g and 0.290 g salts each dissolved in 100 mL of deionized water) was prepared as precursors for Al_2O_3 and ZrO_2 respectively. The previously synthesized Fe_3O_4 (0.600 g) suspension was ultra-sonicated for 10 min and mixed with the solution containing Al_2O_3 and ZrO_2 precursors. The composite solution was adjusted to pH 8.0 using 0.1 M of NaOH and/or 0.01 M of HCl solution. The synthesized composite was stirred by magnetic stirrer under nitrogen atmosphere for 1.5 h at 70 °C. Then, the synthesized composite solution was transferred to beaker and allowed to settle until a clear supernatant solution was obtained followed by the supernatant decanting using permanent magnet. Finally, the product was washed with ultrapure water for several times to remove impurities such as Cl^- and excess OH^- ions.

Coffee spent modified with ($Al_2O_3/Fe_3O_4/ZrO_4$) composites

Synthesis of coffee spent supported ternary metal oxide composite was made according to the method developed by Safarik *et al.* [16-17]. We vary the mass percent ratio of the support to the ternary oxide composite as [50:50, 60:40 and 70:30] to select the one performing better. The coffee spent slurry was prepared in 100 mL of methanol and vigorously stirred by using homogenizer and mixed with the synthesized ternary composite and further washed repeatedly homogenized for 1 h. The coffee spent modified composite was washed with methanol and then air dried [18].

Characterization of the coffee spent modified nanosorbent

The X-ray powder diffractograms of coffee spent (CS), the ternary metal oxide nanocomposite (NC) and coffee spent modified composite (CSMNC) were recorded using Miniflux 11, Rigaku diffractometer with Cu-Kα radiation (λ = 0.1548 nm). SEM images were taken using scanning electron microscope coupled with energy dispersive X-ray spectroscope (SEM-EDX). FT-IR spectra of the coffee spent (CS), nanocomposite (NC) and coffee spent modified composite (CSMNC) were recorded in the range of 400-4000 cm^{-1} using Perkin-Elmer FT-IR spectrophotometer using KBr mull method. Al, Fe and Zr metal ions in nanocomposite (NC) and coffee spent modified composite (CSMNC) were determined using inductively coupled plasma-optical emission spectroscope (ICP-OES).

Batch adsorption studies

The batch adsorption studies were carried out using the prepared coffee spent modified composite employed for adsorption of acidic brown 75 dyes via batch equilibration mode. The adsorbent (1 g) was put in 250 mL Erlenmeyer flask containing 100 mL of acidic brown 75 dye solution equilibrated on an orbital shaker at a speed of 90 rpm at pH 3 with contact time of 120 min and initial concentration of 60 mg/L. The suspension was filtered through a Whatman No. 40 filter paper and the filtrate was analyzed. The dye concentration was determined using double beam UV-Spectrometer, at 465 nm maximum wavelength absorbance. Average values of triplicates measurements were reported. The amount of acid brown dye adsorbed at equilibrium (q_e in mg g^{-1}) was calculated by using the equation 1.

External calibration curve ranging from 5 to 100 mg/L was used for estimation of acid brown 75 dye concentration. The adsorption capacity (q_e) and percentage of removal (R %) were calculated for each run using the following equations (Eqs. (1) and (2));

$$q_e(mg/g) = \frac{[C_i - C_f]V}{m} \tag{1}$$

$$R\% = \frac{(Ci-Cf)}{Ci} * 100 \quad (2)$$

where C_i and C_f are the initial and final concentration of acid brown dye in solution, V is the volume of solution (in liters) and m is the mass of adsorbent (in grams) used.

Optimization of parameters

The effect of adsorbent dosage (0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 g), contact time (0.5, 1, 1.30, 2 and 2.5 h), initial dye concentration (5, 10, 20, 40, 50, 60, 70, 80, 90 and 100 mg/L), speed of agitation (30, 60, 90, 120, 160 rpm) and pH (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) were investigated at values indicated in parenthesis All the experiments were performed in triplicate and the mean value was reported.

Adsorption and kinetic studies

Langmuir and Freundlich isotherms were used for adsorption isotherm study. The isotherm studies were conducted at various initial concentration of acidic brown dyes (2, 4, 6, 8, and 10 mg/L) while maintaining other parameters constant. The kinetics of adsorption was analyzed applying the linear pseudo-first and pseudo-second order kinetic model and the kinetic experimental studies were investigated at 6, 8, and 10 mg/L of acid brown dye while maintaining other parameters constant.

Desorption studies

Desorption study was carried out using acidic brown dye-loaded coffee spent modified composite (1 g) dissolved in 100 mL distilled water. The pH was adjusted by 0.1 M NaOH and 0.1 M HCl up to 5-12 at room temperature, contact time of 30 min with 90 rpm agitation speed. The quantity of desorbed dye was determined by measuring the amount of acidic brown dye in each solution after each desorption process. The desorption rate (D) was calculated using the following equations (Eq.3)

$$\mathrm{D} = \frac{(\mathrm{qi-qt})}{\mathrm{qi}} \quad (3)$$

where q_i and q_t are the acidic brown dye concentrations adsorbed in the coffee spent modified Nanocomposite adsorbent (mg/L) at the beginning of the experiment and after each contact time.

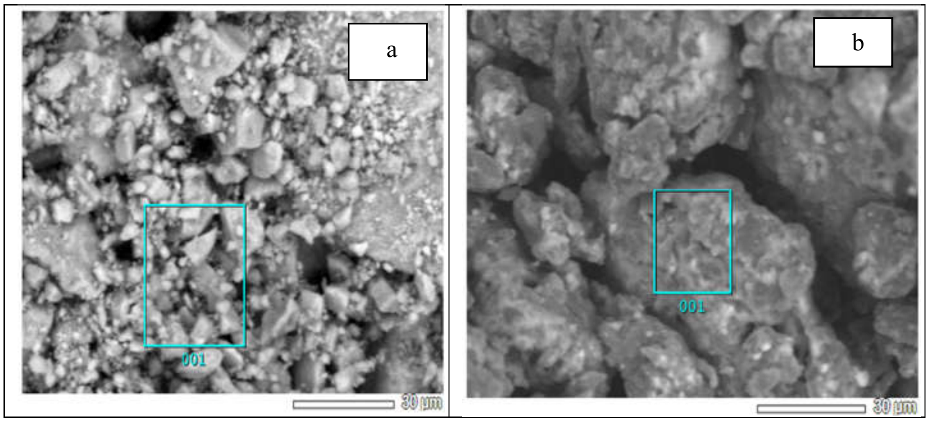
Regeneration study

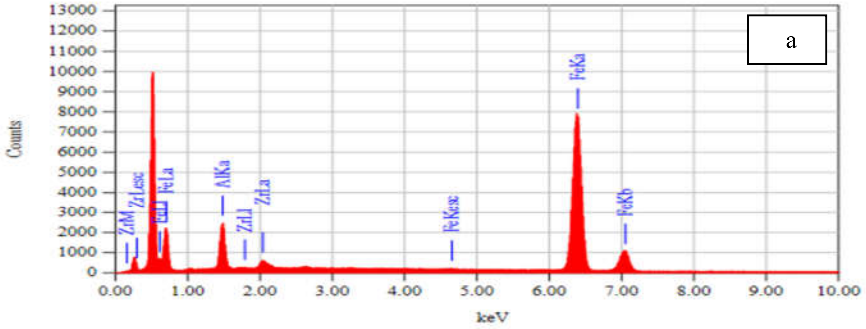
The reusability of the adsorbent was determined at constant feed of 10 mg/L solution acidic brown dye considering the optimum operational parameters such as adsorbent dose (1 g) and time (120 min). This sequential adsorption-desorption process was repeated following the above procedure for 30 min contact time and continuously and washed with distilled water until the pH becomes same as cleaning water.

RESULTS AND DISCUSSION

Characterization of synthesized adsorbent materials

The surface morphology of coffee spent (CS), nanocomposite (NC) and coffee spent modified composite (CSMNC) were conducted using scanning electron microscopy (SEM). The SEM micrographs of the adsorbent materials are shown in Figure 1. As observed in the figure, the coffee spent showed an irregular structure. Zarrinbakhsh *et al.* have reported similar observation [19].





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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3035
Element         (keV)     Mass%     Sigma     Atom%  Compound     Mass%  Cation            K
Al K            1.486      8.04      0.08     15.47                                   4.6063
Fe K            6.398     89.16      0.32     82.93                                  93.4547
Zr L            2.042      2.81      0.08      1.60                                   1.9390
Total                    100.00              100.00
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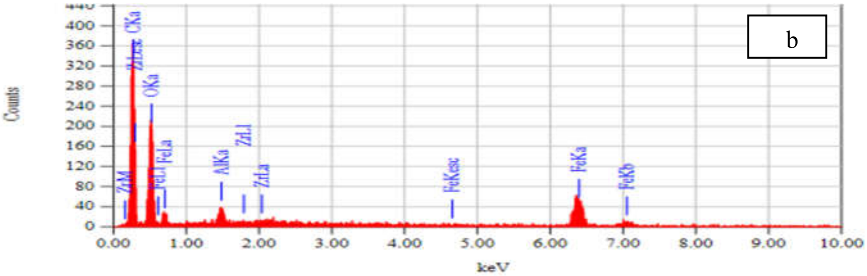

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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2101
Element         (keV)     Mass%     Sigma     Atom%  Compound     Mass%  Cation            K
 C K            0.277     47.46      0.55     58.70                                  41.9214
 O K            0.525     40.70      1.07     37.79                                  40.5197
Al K            1.486      1.23      0.12      0.68                                   1.5467
Fe K            6.398     10.62      0.47      2.82                                  16.0121
Zr L*                        ND                  ND
Total                    100.00              100.00
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Figure 1. Scanning electron microscope (SEM) images and EDX analyses for a) Nano composite and b) Coffee spent modified composite sorbents.

The SEM image of coffee spent modified composite (CSMNC) adsorbent has shown no distinct morphology yet with well-developed cavernous porous structure. Moreover, the elemental composition studies using EDX showed the percentage atomic composition of Al, Fe and Zr 8.0%, 89.2% and 2.8%, respectively. The EDX elemental composition confirmed the presence of all expected metals in the ternary nanocomposite adsorbent system. This reveals the successful modification of coffee spent with ternary nanocomposite in the mixed mass ratio. On the other hand the SEM micrograph of coffee spent modified composite (CSMNC) adsorbent indicates the ensuing elemental percentage atom composition; 47.5% C, 40.7% O, 1.2% Al, 10.6% Fe.

XRD patterns of the ternary system $Al_2O_2/Fe_3O_4/ZrO_2$ and the coffee spent modified composite (CSMNC) adsorbent are presented in Figure 2. The diffraction peaks observed at 2θ (degree) values of 18.54, 30.48, 35.92, 43.38, 57.26, 63.10, and 74.49, for the naked nanocomposite, are ascribed to a face centred cubic spinel structure of pure magnetite (Fe_3O_4) [JCPDS: 96-900-5840]. No diffraction peaks were observed for alumina and zirconia due to the amorphous nature of these oxides (at the temperature of synthesis). In addition, these elements appeared in lower concentration (i.e. 25% for Al and 5% for Zr). The literature review indicates that the XRD of crystallized alumina such as γ-Al_2O_3 might present under thermal treatment of more than 600 °C with the concentration higher than 30% [20]. The XRD peaks were observed for coffee spent modified composite at diffraction angle 2θ of 35.2°, 42.7°, 57.2° and 62.6° attributable to face centered cubic spinal structure of pure magnetite (Fe_3O_4), a component of the nanocomposite supported onto the coffee spent powder. The typical diffraction peak shown at 2θ values of 20.18° and 21.98° represent crystalline cellulose in the coffee spent [21]. The peak shift observed ascribes the formation of the heterostructure upon composite formation.

The average crystallite sizes (D) of the nanocomposite and coffee spent modified composite sorbents were calculated by using Scherrer Equation, $D = K\lambda/\beta.\cos\theta$, [23]. The average crystallite sizes (D) of the nanocomposite is found to be in the range of 7.3-8.4 nm, the size at the maximum intensity being about 7.52 nm. Previously, similar results have been reported [14, 22]. The value of average crystallite sizes (D) of coffee spent modified nanocomposite was in the range of 60.7-52.7 nm, the size for the highest intensity peak being around 52.9 nm.

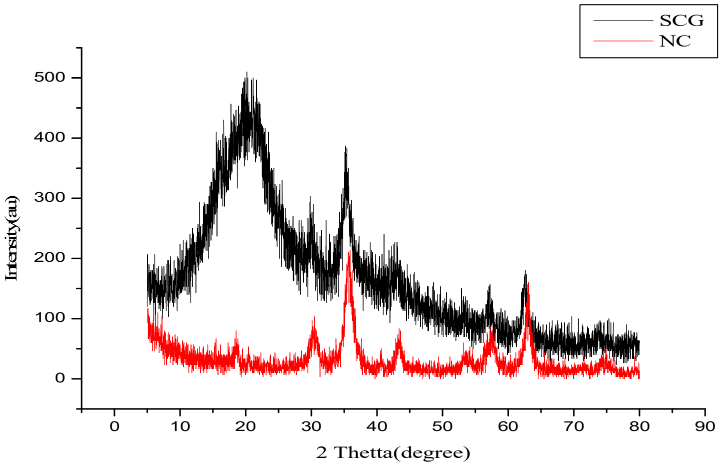

Figure 2. XRD patterns of a) Nanocomposite and b) coffee spent modified nanocomposite.

The FT-IR spectra of coffee spent, the bare nanocomposite and coffee spent modified composite are shown in Figure 3. The FT-IR spectra of coffee spent shows a broad band peak at 3570-3250 cm^{-1} assigned to the stretching of major O-H functional groups and minor N-H groups (John, 1996). The peaks at 2920 and 2850 cm^{-1} are due to asymmetric and symmetric C-H stretching vibrations for methyl and methylene groups attributed to caffeine and lipids. The strong aromatic nature of the compounds is confirmed by a series of peaks within the 1022–567 cm^{-1} range, signalling the possible presence of additional C-H groups with aromatic out-of-plane bend. Phenol or tertiary alcohol with O-H bend was also observed by a reading of 1384 cm^{-1}.

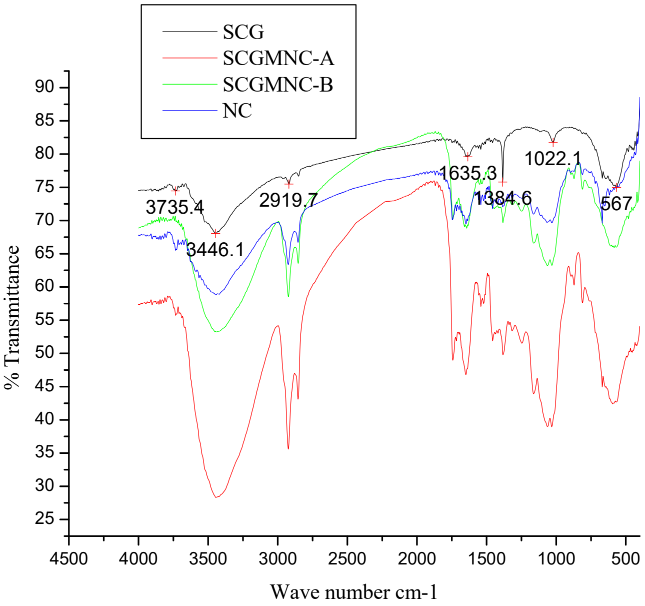

Figure 3. FTIR spectra of a) coffee spent (SCG), b) nanocomposite (NC) and c) coffee spent modified nanocomposite before (SCGMNC-B) and d) after (SCGMNC-A) adsorption.

For the bare nanocomposite, the predominant band appearing around 3445 cm^{-1} is attributed to stretching vibrations of the O-H groups and the peak around 1628 cm^{-1} correspond to H–O–H bending vibrations of the physically adsorbed water molecules and to the bending vibration of Zr–OH groups. Bands exhibited at 2923 and 2853 cm^{-1} represent C–H stretching and anti-symmetrical and symmetrical H–O–H stretching vibrational modes. The peak observed at 1384 cm– might be emerged from N–N stretching due to surface adsorption of N_2 gas used during the synthesis of magnetite. Stretching frequencies below 1000 cm^{-1} in general could be ascribed to M-O bonds of the composite [24-25, 37]. The supported composite exhibited a spectrum comprising both components evidencing the formation of the same. The only difference noted is the intense signals for the after sorption cases possibly due to presence of moisture and functional groups that are associated with the dye.

ICP-OES was used to determine the concentration of each metal present in the nanocomposite adsorbent. The result is presented in Table 1. The percent by weight ratios for Fe, Al and Zr found in the adsorbents confirmed the homogenized distribution and modification of the adsorbent.

Table 1. Elemental composition of Nano composite (NC) and coffee spent modified with Nanocomposite (CSMNC).

Adsorbent material	Metal ion	Average concentration (mg/L)	Concentrations metal in adsorbent (mg/kg)	% ratio	% recovery Average
CSMNC	Al	0.10577	6.167	21.14%	84.0 ± 0.009
	Fe	0.34807	20.745	71.10%	94.6 ± 0.01
	Zr	0.04037	2.266	7.77%	66.9 ± 0.02
NC	Al	1.16503	51.12	14.70%	98.3 ± 0.03
	Fe	5.89019	258.95	74.5%	98.82 ± 0.04
	Zr	0.85756	37.5	10.80%	97.72 ± 0.02

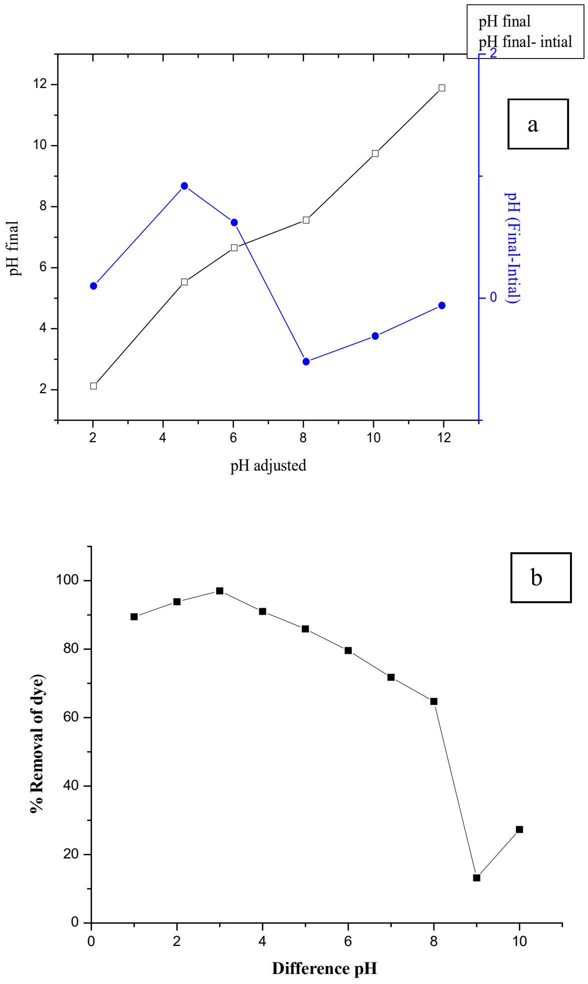

Figure 4. a) Effect of pH on the removal of acidic brown 75 dyes (doze = 1 g; Agitation speed = 70 min; C_i = 60 mg/L; T = 90 min); b) pHpzc of the composite sorbent.

Effect of contact time and adsorbent dosage

The effect of contact time on adsorption process was investigated taking 30, 60, 90, 120, and 160 min time intervals (data not shown). The percentage removal of acidic brown dye increased up to 120 minutes with maximum adsorption efficiency of about 96% beyond which there was no further change. The decrease in adsorption efficiency was due to deposition of dyes on the available adsorption site on adsorbent material and a state of dynamic equilibrium with the amount of the acidic dye adsorbed onto the adsorbent [24]. The effect of adsorbent dosages was investigated at 0.1, 0.5, 1, 1.5, 2, and 2.5 g in 100 mL of acidic brown dye solution maintaining the other experimental conditions constant. From the analysis, it was found that the percentage adsorption removal has become increased from 71.9% to 96.9% respectively with increase of the amount of adsorbent from 0.1 g to 2.5 g. In the adsorbent dosage range of 0.1-1.0 g, the rate of percentage acidic brown dye removal sharply increased and become constant onwards. Therefore, 1.0 g of adsorbent was taken as optimum amount for further studies. A similar observation has been reported before [31].

Effect of initial dye concentration

The influences of initial concentrations on the dye removal was determined using different initial concentrations of acid brown 75 dye and the results are depicted in Figure 5. The initial dye concentration study showed that the removal of acidic brown 75 dyes decreased from 96.3 to 57.1% as initial concentration of the dye increased due to the saturation of adsorption surface sites on the adsorbent [30]. Therefore, 10 mg/L initial concentration of acidic brown 75 dyes was taken as the optimum concentration.

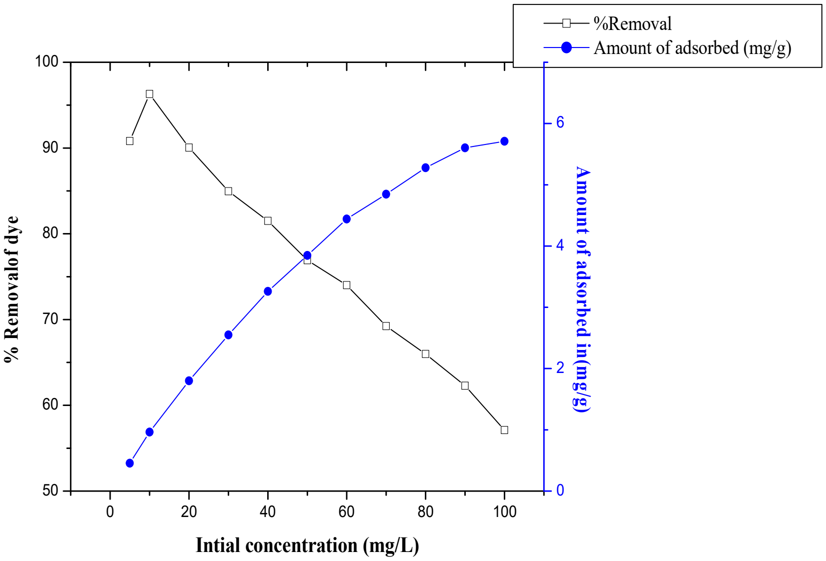

Figure 5. The effect of initial concentration of acid brown 75 dye on its removal by the adsorbent (CSMNC): dosage = 1 g; temperature = 25 ± 2 °C; pH = 5.6; agitation speed = 90 rpm; Contact time = 2 h.

Adsorption isotherms

The Langmuir and Freundlich adsorption isotherm models were used to investigate the interaction of adsorbate and the adsorbent. The Langmuir and Freundlich adsorption isotherm are given in Eq. (4) and (5), respectively:

$$\frac{C_e}{\mathrm{q_e}} = \frac{C_e}{Q_o} + \frac{1}{K_L.Q_o} \tag{4}$$

$$\log(\mathrm{q_e}) = \log(\mathrm{K_F}) + \frac{1}{n}\log(C_e) \tag{5}$$

where q_e (mg g^{-1}) is the adsorbed amount of pollutant per adsorbent unit mass and C_e (mg L^{-1}) is the adsorbate concentration at equilibrium. K_L (L mg^{-1}) and K_F (L mg^{-1}) are Langmuir and Freundlich constants, respectively. q_e (mg g^{-1}) is the concentration at equilibrium and $1/n$ is the heterogeneity factor in Freundlich models.

The Langmuir and Freundlich constants are depicted in Table 2. In the case of Langmuir model, the maximum adsorption capacity (q_{max}) by coffee spent modified nanocomposite was 8.396 mg/g and the regression coefficient was 0.9996. Whereas in the case of Freundlich model, the maximum adsorption capacity of coffee spent modified nanocomposite was 6.917 mg/L with the regression coefficient of 0.9575. Comparison of the isotherm models could be achieved through analyzing the values of regression coefficients (R^2) and the result showed that Langmuir isotherm models can better describe the adsorption of acid brown 75 dye onto coffee spent modified nanocomposite. This reveals that molecule of acidic brown 75 dyes were adsorbed on each site of adsorbent although heterogeneity of the adsorbent surface cannot be underestimated given the regression coefficient obtained for the Freundlich isotherm.

Furthermore, the Langmuir isotherm is expressed in terms of dimensionless equilibrium parameter (i.e. R_L). The dimensionless constant of equilibrium parameter (R_L) that is given in equation 6 is used to express the fundamental characteristics of the Langmuir isotherm [33].

$$R_L = \frac{1}{(1+C_o K_L)} \tag{6}$$

where: C_0 represent the highest initial concentration of adsorbate (mg/L). R_L can take values between 1 and zero. The value of R_L indicates the situation of the isotherm to be linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [34]. The result showed that there was a decrease in R_L value from 0.580 to 0.216 while increasing the acidic brown dye concentration. This indicates that increased affinity between adsorbate and adsorbent. Moreover, the value of R_L is found to be very near to zero indicating that the adsorption of acid brown dye onto the coffee spent modified nanocomposite is exceedingly favorable adsorption process.

Table 2. Langmuir and Freundlich isotherm constants for adsorption of acid brown 75-dye dye by coffee spent modified Nanocomposite adsorbent.

Langmuir isotherms			Freundlich isotherm		
q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
8.396	6.236	0.9996	6.917	2.76	0.9498

Adsorption kinetics

The linear pseudo-first order and pseudo-second order models adsorption kinetics were used for adsorption of acid brown dye onto coffee spent modified nanocomposite. The linear pseudo-first order and pseudo-second order and kinetic model equations are shown in Eq. (7) and (8), respectively [24].

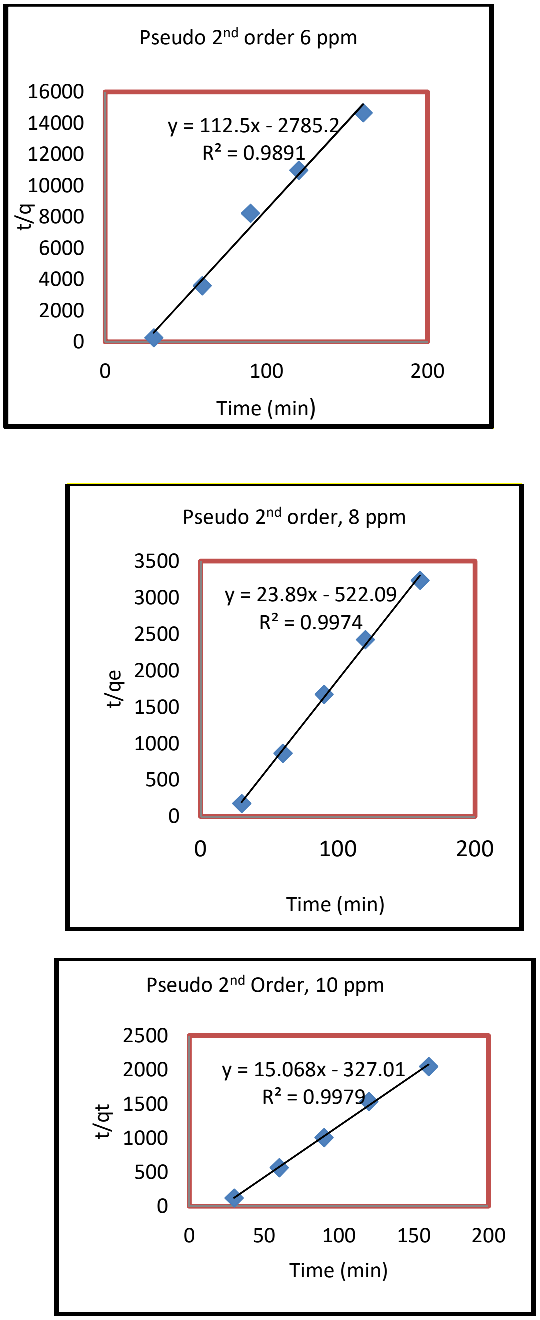

Figure 6. Linear pseudo-second-order kinetic model plot for adsorption acid brown 75 dye: adsorbent dosage = 1 mg; temperature = 25 ± 2 °C; pH = 3.

Pseudo-first-order kinetics model

$$\log(q_e - q_t) = \log(\mathrm{q_e}) - \frac{K_1}{2.303} \qquad (7)$$

Pseudo-second-order kinetics model can be expressed as:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{k_2 \cdot q_e{}^2} + \frac{\mathrm{t}}{q_e} \qquad (8)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_t (mg/g) is the amount of dye adsorbed at time t. k_1 (1/min) and k_2 (g/mg.min) represent the pseudo-first and pseudo-second order rate constants, respectively.

The plots of linear pseudo-first and pseudo-second-order kinetic models have resulted to the following kinetic parameters illustrated in Figure 6 and Table 3. The best-fit model was selected based on the match between experimental q_e ($q_{e,exp}$) and theoretical q_e ($q_{e,cal}$) values and the values for linear regression coefficient (R^2) at the studied conditions. It can be seen from the table that the experimental q_e ($q_{e,exp}$) values are in good agreement with the theoretical q_e ($q_{e,cal}$) values in the case of pseudo-second order kinetic model for adsorption of acid brown dye onto the coffee spent modified nanocomposite.

Besides, the value of the regression coefficients (R^2) of the fitted linear kinetic model is close to unity for pseudo-second order kinetic model than pseudo-first order kinetic model. It is therefore concluded that kinetics for adsorption of acid brown dye onto coffee spent modified nanocomposite obey the pseudo-second order kinetic model. The pseudo-second order model assumes that the rate-limiting step is chemisorptions [34]. So, we can deduce that the dye ions and adsorbent are connected though electrostatic interaction [35].

Table 3. Linear kinetic parameters for adsorption of acid brown dyes onto coffee spent modified nanocomposite adsorbent.

Acid brown dye							
Pseudo first order					Pseudo second order		
Initial concentration (mg/L)	$q_{e,\ exp}$ (g/g)	$q_{e,\ cal}$ (mg/g)	k_1 (g/mg.min)	R^2	$q_{e,\ exp}$ (mg/g)	k_2	R^2
6	0.493	0.513	0.006	0.5274	0.493	4.545	0.9891
8	0.630	0.630	0.006	0.5806	0.624	0.915	0.9974
10	0.758	1.201	0.008	0.5788	0.753	2.271	0.9979

Desorption study

Desorption of acidic brown dye from the adsorbent surface of coffee spent modified nanocomposite was investigated in the pH range from 5-12. It's observed that as the solution pH increases the efficiency of desorption of dyes from coffee spent modified nanocomposite also increases (data not shown). The maximum percentage desorption (i.e. 94.3%) of acidic brown dye from the adsorbent material was observed at pH 9.

Regeneration cycle

The regeneration of the coffee spent modified nanocomposite adsorbent materials for reuse purpose was investigated by conducting sequential adsorptions/desorption cycles. The adsorbent regeneration was very fast and effective. As observed in Figure 7, the adsorption percentages decreased from 96.19% (first cycle) to 57.14% (eighth cycle) and the percentage desorption was decreased from 94.29 to 46.67% though out the eight cycles [18]. The decrease in adsorption efficiency of the adsorbent material after successive reuse was due to saturation of the active adsorbent sites, degradation of adsorbent at different pH conditions, and progressive blockage of the active adsorbent sites. However, as it can be seen in Figure 9, the adsorbent could be reused efficiently four times with an efficiency of 80%. Thus, from the recycle studies it can be concluded that coffee spent modified Nano composite has a very good regeneration and reusability capacity.

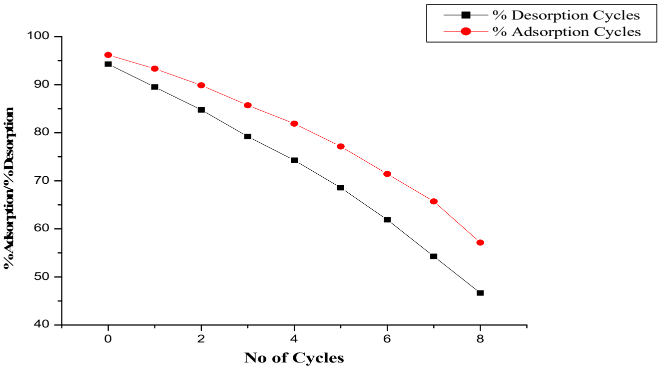

Figure 7. Number of adsorption and desorption cycles.

CONCLUSION

In this study bio-supported ternary $Al_2O_2/Fe_3O_4/ZrO_2$ composite was prepared to assess its dye removal capacity. The crystal structure, composition, morphology and functional group of the as-obtained materials were characterized using XRD, ICP-OES, SEM-EDX, and FTIR, respectively. The effect of initial dye concentration, contact time, adsorbent dosage and pH were explored and an optimum values of 10 mg/L, 120 min, 1 g and 3 were obtained, respectively. Under the optimized conditions, the bio-supported ternary composite adsorbent exhibited an adsorption capacity above 95%.

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