Article

Optimization of Fe@Cu Core–Shell Nanoparticle Synthesis, Characterization, and Application in Dye Removal and Wastewater Treatment

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Abstract: Green synthesis of core–shell nanoparticles is gaining importance nowadays as it is viewed as being environmental friendly and cost effective. The present study aimed to synthesize iron@copper core–shell nanoparticles using a polysaccharide-based bioflocculant from *Alcaligenes faecalis* and to evaluate its efficiency in dye removal and river water and domestic wastewater treatment. The synthesized samples were characterized by Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, transmission electron microscopy, and UV-Vis spectroscopy analysis. To optimize the best concentration for core–shell formation, different ratios of iron to copper were prepared. Sample 1 (S1) contained 1:3 iron to copper (Fe 25%–Cu 75%), sample 2 (S2) contained 1:1 iron to copper (Fe 50%–Cu 50%), and the third sample (S3) contained 3:1 iron to copper (Fe 75%–Cu 25%). The flocculation activity (FA) was above 98% at 0.2 mg/mL for all the samples and the samples flocculated well under acidic, alkaline, and neutral pH conditions. Sample 3 was shown to be thermostable, with flocculation activity above 90%, and samples 2 and 1 were also thermostable, but the flocculation decreased to 87 at 100 °C. All three samples revealed some remarkable properties for staining dye removal as the removal efficiency was above 89% for all dyes tested. The synthesized core–shell nanoparticles could remove nutrients such as total nitrogen and phosphate in both domestic wastewater and Mzingazi river water. Furthermore, high removal efficiency for chemical oxygen demand (COD) and biological oxygen demand (BOD) was also observed.

Keywords: core–shell nanoparticles; removal efficiency; optimization; synthesis

1. Introduction

Drinking water scarcity, i.e., water free of pathogens and toxic chemical substances, is a worldwide problem due to population growth, extended droughts, competing demands from different users, and more health-based regulations. However, the conditions are very severe in developing countries [1]. Chemical flocculants are widely used nowadays owing to their low-cost, effective flocculation performance. However, their application has been found to cause environmental and health hazards such as Alzheimer’s disease [2]. Use of bioflocculants has gained interest in recent years due to the biodegradability properties bioflocculants possess and their negligible environmental hazards. Nonetheless, higher production costs and low flocculation yields are limitations to the industrial application of bioflocculants [3]. Consequently, in recent years research has mainly focused on the synthesis of nanoparticles from bioflocculants and their application in industrial effluents and

wastewater treatment. Alternatively, composite flocculants serve as a way to reduce cost as they can flocculate well even at low dosages and reduce the risk of adverse effects that come with synthetic flocculants since their dosage is reduced to the smallest possible [3].

Textile industries discharge tons of effluents to the environment which contain pollutants and dyes that are carcinogenic in nature and non-degradable [4]. Furthermore, most of the paper and textile industries use dyes and discharge the effluents to water resources. Technologies such as hydrogen peroxide and UV radiation are not effective in relation to these dyes as they are chemically stable. Recent findings suggest that nanomaterials can be successfully used in dye degradation, making nanoparticles to be more profitable compared to chemical and physical methods [4]. Furthermore, copper nanoparticles have been found to be effective in wastewater treatment. They have been found to be able to remove up to 88% and 90% of chemical oxygen demand (COD) and biological oxygen demand (BOD), respectively, in mine wastewater, domestic wastewater, and river water [5]. Similarly, iron oxide nanoparticles have been widely applied in the removal of chemical pollutants from water in a separation process known as adsorption [6].

In the present study, iron@copper core-shell nanoparticles are synthesized using a bioflocculant from marine species *Alcaligenes faecalis*. The bioflocculant which is used for synthesis is composed of mainly carbohydrates. Copper sulphate (CuSO_4) and iron chloride (FeCl_3) are used as the precursors for the iron@copper nanoparticles. Different ratios of iron to copper (1:3, 1:1, and 3:1) are prepared to optimize the most effective combination. Various parameters such as dosage, pH, temperature, and cations are varied to optimize the effectiveness of the synthesized iron@copper core-shell nanoparticles in flocculation efficiency and are tested against kaolin clay as a standard test material.

2. Results

2.1. X-Ray Diffraction Studies of S1, S2, and S3

X-ray diffraction patterns of samples S1, S2, and S3 are shown in Figure 1. Strong and characteristic crystalline peaks are observed between 30° and 50° 2θ .

Figure 1. X-ray diffractograms of samples (a) S1, (b) S2, and (c) S3.

2.2. FT-IR Spectra of S1, S2, and S3 Nanoparticles

Figure 2 shows the functional groups that are present in S1, S2, and S3. Figure 2 indicates the presence of a hydroxyl (-OH) group at 3250 cm^{-1} and an amine (-NH₂) group at 1750 cm^{-1} in the samples. The weak band at 2244 cm^{-1} for all samples can be attributed to the presence of aliphatic bonds.

Figure 2. FT-IR spectra of samples (a) S1, (b) S2, and (c) S3.

2.3. Morphological Studies of S1, S2, and S3 Using SEM

Figure 3 shows SEM images of samples S1, S2, and S3. Granular-like morphology is evident from Figure 3 for all three samples.

Figure 3. Cont.

Figure 3. SEM images of samples (a) S1, (b) S2, and (c) S3.

2.4. Elemental Analysis of S1, S2, and S3 Using SEM-Energy-Dispersive X-Ray Analysis (EDX)

Table 1 represents SEM-EDX results of samples S1, S2, and S3. The wt.% of the elements C, O, Na, Mg, P, S, Cl, Ca, Fe and Cu present in the samples S1, S2, and S3.

Table 1. Energy-dispersive X-ray analysis (EDX) of samples (a) S1, (b) S2, and (c) S3.

Elements	Sample		
	S1 (wt.%)	S2 (wt.%)	S3 (wt.%)
C	13.74	19.07	16.27
O	53.97	55.09	54.14
Na	8.53	7.01	8.22
Mg	14.10	12.27	12.42
P	1.30	0.63	0.94
S	0.39	-	0.38
Cl	0.17	0.20	0.08
Ca	1.34	0.70	0.76
Fe	1.65	1.19	0.83
Cu	4.82	3.83	5.96
Total	100.00	100.00	100.00

2.5. The Effect of Various Metal Ratios in the Flocculation Process

Figure 4 shows the effect of various samples with different proportions of iron to copper on flocculation activity. The first sample (S1) contained 1:3 iron to copper (Fe 25%–Cu 75%), sample 2 (S2) contained 1:1 iron to copper (Fe 50%–Cu 50%), and the third sample (S3) contained 3:1 iron to copper (Fe 75%–Cu 25%). All the samples (S1, S2, and S3) were found to flocculate best at the lowest concentration of 0.2 mg/mL.

Figure 4. Dosage effect on flocculation activity of nanoparticle samples S1, S2, and S3.

2.6. Effect of pH on the Flocculation Process

Figure 5 shows the effect of pH on the flocculation activity of different samples with different proportions of iron to copper (Fe 25%–Cu 75% for S1, Fe 50%–Cu 50% for S2, and Fe 75%–Cu 25% for S3). All samples indicated that they are able to flocculate under extremely acidic and extremely basic pH with flocculation activity above 95%.

Figure 5. pH effect on the flocculation activity of nanoparticle samples S1, S2, and S3.

2.7. The Effect of the Presence of Different Metal Ions in the Flocculation Process

Table 2 represents the effect of cations on samples S1, S2, and S3 with regard to flocculation activity. All the samples were found to be able to flocculate effectively in the absence of cations, with flocculation activity found to be above 95%.

Table 2. Effect of cations on flocculation activity of nanoparticles.

Type of Flocculant	Cation FA (%) $\pm$ SD			
	Control	Na ⁺	Ca ²⁺	Fe ³⁺
S3	95 $\pm$ 0.031 ^a	97 $\pm$ 0.012 ^a	99 $\pm$ 0.025 ^a	97 $\pm$ 0.037 ^a
S2	96 $\pm$ 0.003 ^a	95 $\pm$ 0.063 ^a	98 $\pm$ 0.007 ^a	87 $\pm$ 0.023 ^b
S1	96 $\pm$ 0.039 ^a	95 $\pm$ 0.051 ^a	98 $\pm$ 0.012 ^a	97 $\pm$ 0.014 ^a

Values represent mean $\pm$ deviation of replicate readings. Percentage flocculation activities with different letters (a and b) are significantly ($p < 0.05$) different. Legend: FA, flocculation activity.

2.8. Thermostability Test for Samples S1, S2, and S3

Figure 6 represents the effect of temperature on flocculation activity. All the samples were shown to be thermostable, with flocculation above 80% at 100 °C. Sample 3 was the most stable with a flocculation activity of 93%.

Figure 6. Effect of temperature on flocculation process of samples S1, S2, and S3.

2.9. The Removal Efficiency of Staining Dyes by Nanoparticle Samples S1, S2, and S3

Figure 7 shows the removal efficiency of staining dyes by nanoparticle samples S1, S2, and S3. All the samples showed an excellent ability to remove the staining dyes. Sample 3 had an efficiency of above 90% for the four dyes (safranin, methylene blue, methylene orange, and malachite green) which were examined.

Figure 7. Removal efficiency of dyes by nanoparticle samples S1, S2, and S3.

2.10. Removal Efficiency of Nutrients in Wastewater by Nanoparticle Samples S1, S2, and S3

Table 3 shows the removal of COD, BOD, phosphate and total nitrogen in Vulindlela wastewater and Mzingazi River water by nanoparticle samples S1, S2, and S3. S3 was observed to be the most effective in removing both phosphate and total nitrogen, with a removal efficiency of above 97%.

Table 3. Removal of pollutants in Vulindlela wastewater and Mzingazi River by nanoparticle samples S1, S2, and S3. Legend: COD, chemical oxygen demand; BOD, biological oxygen demand.

Type of Flocculant	Type of Wastewater	Type of Pollutants								Removal Efficiency (%)			
		Water Quality Before Treatment				Water Quality After Treatment				COD	BOD	P	N
		COD mg/mL	BOD mg/mL	P mg/mL	Total nitrogen mg/mL	COD mg/mL	BOD mg/mL	P mg/mL	Total mg/mL	-	-	-	-
S1	Domestic	2.313	123	3.38	0.223	1.151	17	2.55	0.017	50	86	37	88
	Mzingazi river	3.300	146	85.7	0.127	1.074	15	0.120	0.020	67	87	99	84
S2	Domestic	2.313	123	3.38	0.223	1.152	13	0.69	0.124	50	89	80	44
	Mzingazi river	3.300	146	85.7	0.127	1.900	21	0.121	0.025	42	86	99	80
S3	Domestic	2.313	123	3.38	0.223	0.464	19	0.09	0.014	85	91	97	98
	Mzingazi river	3.300	146	85.7	0.127	0.793	31	0.109	0.023	79	72	99	82

3. Discussion

In Figure 1 the strong peaks can be observed at 20–35°, 40°, and 65° for S1. Contrary to this, it can be noted that the strongest peaks were at 20–35°, 45°, 65°, and 77° for S2. In S3, the strongest peaks can be observed at 20–22° and 30°. However, these peaks are not as strong as those seen in S2. Strong peaks normally represent crystallinity and smaller particle size. It can be observed that the S3 diffractogram behaves differently from those of the other two samples. This might be attributed to the synergistic effect that results from the changed sample composition.

It can be deduced that when the proportion of iron to copper is 1:3 the size of the as-synthesized Fe@Cu core–shell nanoparticles become smaller. Different functional groups serve as the binding sites for flocculants during the flocculation process [7]. Higher flocculation ability of the samples can be attributed to the presence of different functional groups as observed in Figure 2. Different functional

groups were revealed by FT-IR spectroscopy analysis. Hydroxyl (-OH) and amine (-NH₂) groups were observed in the same plane for samples S1 and S2, respectively. The amine group could have originated from the bioflocculant that was used [7]. The peaks at 1700–1500 cm⁻¹ signify the presence of a C=O amide group and the deep peak in the 1200 cm⁻¹ region is typical of C-OH stretching. C-O-C stretching can be observed at 1250–1050 cm⁻¹ as depicted in Figure 2. The strong peak in sample S2 at 500 cm⁻¹ is typical of C-Cl; this was also confirmed by the presence of Cl in the SEM-EDX analysis.

The morphology of S1, S2, and S3 as observed under SEM are shown in Figure 3. A change in morphology was observed and the proportion of iron to copper also changed. S1 had a rough amorphous-like structure with granules and in S2 the structure was similar to that of S1 but with much smaller granules. Contrary to this, S3 had a smooth amorphous structure with big granules, which signifies a structural transition as the ratio of iron to copper was varied. SEM-EDX analysis of samples S1, S2, and S3 showed different elements that are present. From Table 1 (sample S1) elements such as O, Mg, and Na can be seen to be abundant in huge percentages, with oxygen having 53.97 wt.%, magnesium 14.10 wt.%, and Na 8.53 wt.%. Cu was the fourth highest element, having over 4 wt.%, while Fe had 1.65 wt.%. The first three elements, which are present in abundance, could owe their abundance to the results of the culture medium which was used to grow the microorganism for bioflocculant production. From Table 1 (sample S2), elements such as O, Mg, Na, Cu, and Fe can be seen to be the most dominant in sample S2, with oxygen, magnesium, and sodium making up 74.37 wt.% combined. This is due to the fact that these elements form part of the structure of the biomolecule (bioflocculant) which was used during synthesis, and, also, the fact that the medium which was used for bioflocculant production consist of these elements. Lastly, in sample S3 (Table 1) a significant increase in Cu is observed in comparison to the other two samples. However, O, Mg, and Na are still present in high proportions, just like in the rest of the samples.

UV-Vis spectroscopy and TEM and TGA analysis were also performed on these materials. UV-Vis spectra revealed plasmon resonance (SPR) spectra with an absorbance range of 295–500 nm; the peak maxima for the synthesized particles was observed at around 300 nm (Figure S1). TEM images show that the higher aggregation of particles could be due to the surfactant (bioflocculant) matrix (Figure S2). The inset TEM image also indicates the extent of aggregation (Figure S2). Selected area electron diffraction on the iron@copper core-shell nanoparticles failed to show any discernible electron diffraction, indicating that the iron@copper core-shell nanoparticles are amorphous. In the TGA analysis, all three samples seemed to be shown to be thermostable, as they retained over 50% of their weight at over 800 °C (Figure S3).

Sworska et al. [8] have posited that there are various flocculation mechanisms but that flocculation by bridging is the most important. Adsorption of flocculant segments onto the surface of more than one particle is described as bridging. In sample S1 it was found that flocculation activity remained almost constant, being 98% for the range 0.2–0.6 mg/mL, suggesting that the optimum dosage used for bridging to occur should be below 0.8 mg/mL. The best flocculation is observed at flocculant dosages corresponding to particle coverage that is significantly less than complete [8]. In S2, the flocculation activity fluctuated for the range 0.4–0.8 mg/mL, as observed in Figure 4, which could be due to the synergetic effect between the iron and copper metal ions. A similar trend as in S1 was also witnessed in S3: the flocculation activity remained almost the same for the range 0.2–0.6 mg/mL, and it started to decrease at 0.8 mg/mL. The effect of pH on flocculation activity was evaluated in accordance with a description by Zaki et al. [9] where 1.0 M HCl and 1.0 M NaOH were used for pH adjustment whenever necessary. All the samples could flocculate best under all pH conditions (acidic, neutral, and alkaline) with above 90% flocculation. As presented in Figure 5, the optimal flocculation activity was achieved at neutral pH; however, the flocculation activity was still above 90% for both under acidic and alkaline conditions, suggesting that the nanoparticles are pH stable. The absorption of H⁺ ions tends to weaken the nanoparticle-kaolin complex formation at acidic and alkaline pH [9]. This remarkable property of iron@copper core-shell nanoparticles to withstand acidic and alkaline pH could be contributed to by the ability of core-shell nanomaterials to withstand harsh conditions

which is brought about by the relationship between the core and the shell [10]. These nanoparticles are of commercial value, as they can flocculate acidic and alkaline water. Cations enhance flocculation activity by balancing the negatively charged kaolin suspension and that of the functional group of the flocculants [11]. Equally, monovalent, divalent, and trivalent cations could enhance the flocculation process. However, in this case, the synthesized nanoparticles proved to be independent of cations, as the flocculation was above 95% when there were no cations added. The limitations of bioflocculants are their high production cost and low flocculation efficiency as compared to their counterpart synthetic flocculants; some of the bioflocculants require cations to work effectively. These findings suggest that the synthesized iron@copper core-shell nanoparticles could be cost-effective as their flocculation activity was found to be above 95% in the absence of cations. As depicted in Table 2 above, both S1 and S2 flocculate best with Fe^{3+} ; however, the results show that the difference between the control and Fe^{3+} is not significant. Sample 3 showed a decreased flocculation activity when Fe^{3+} was added, suggesting that the sample works better in the absence of cations. The effectiveness of samples S1, S2, and S3 when heated at high temperatures was examined for the temperature range 60–100 °C. The samples were subjected to high temperatures in a water bath for 30 min before the flocculation activity was measured. The flocculation activity of all the samples remained almost the same for the range 60–80 °C and started to decrease when the temperature was increased to 100 °C. Sample 3 was found to be the most stable of the three samples, with the flocculation activity remaining above 90% even when the sample was subjected to the higher temperature of 100 °C. Contrarily, samples S1 and S2 revealed a slight decrease in flocculation activity when they were exposed to the high temperature of 100 °C, with flocculation activity decreasing from 97 to 87%. Giri et al. [12] have reported a thermostable bioflocculant which maintains up to 89% flocculation activity at the high temperature of 100 °C. Most bioflocculants which are composed mainly of carbohydrates and of few proteins are able to withstand high temperatures [12]. The bioflocculant which was used for synthesis was composed mainly of carbohydrates, which could be the reason for the high thermostability of the nanoparticles studied here, and literature suggests that such bioflocculants are thermally stable [9]. Moreover, core-shell nanoparticles are said to be able to withstand extreme conditions due to the synergistic effect between the core and the shell [13].

Treatment of some discharged effluents from some industries is still a serious issue, as some of these discharges contain colorful dyes [14]. The pharmaceutical, leather, paper, textile, sugar, cosmetic, food, and printing industries are the most common discharging industries. These colorful dyes have serious impacts on ecosystems, with the dyes preventing light penetration within rivers and at the bottom of lakes and ponds, hindering photosynthesis in plants. Moreover, they may also lead to anaerobic conditions that can be fatal to aquatic life. As presented in Figure 7 above, the samples were prepared by mixing 4 g of dye in 1 liter of distilled water, and 100 mL of the dye solution was mixed with 2 mL of 0.2 mg/mL of nanoparticle solution (S1, S2, and S3). The mixture was agitated for a minute and transferred to a graduated measuring cylinder, and then left to stand for 5 min before it was analyzed using a spectrophotometer. The nanoparticles were very effective in relation to staining dye removal and the efficiency was above 89% for all for just a 5 min contact time. Vulindlela is a domestic wastewater treatment plant and is located within the locality of the University of Zululand. The plant treats water before it is discharged to the surrounding streams. It is of the utmost importance to treat water before it is discharged as some of the surrounding community uses the streams' water for domestic crop farming purposes. As shown in Table 3, sample S3 was the most effective in removing both phosphate and total nitrogen while samples S1 and S2 could only remove total nitrogen and phosphate, respectively. For the removal of COD in the wastewater, both samples S1 and S2 were not so effective, with merely a 50% removal efficiency observed. Contrary to this, sample S3 was the most effective, with 80% COD removal. Mzingazi River is geographically located around the city of Richards Bay, which has a high activity of industrialization and sugarcane farming. This accounts for the high phosphate content in the water, as some phosphate is washed by rain from farming fertilizers and industries into the river. Excess accumulation in water has an adverse impact on aquatic life;

it may cause “brown blood diseases” in fish or it may result to eutrophication [15]. Table 3 shows results for the samples that were able to remove up to 99% of phosphate when it was left to stand for one week; over 80% of total nitrogen was removed when the samples were prepared following the manufacturer’s instructions on the test kit. Hence, it can be deduced that for nanoparticles to give an optimum removal efficiency for phosphate, the samples should be allowed a longer contact time. With regard to COD removal, samples S1 and S3 were able to remove 67% and 79%, respectively, while sample S2 could only remove 42% of COD from the water. In Table 3, all the samples, i.e., S1, S2, and S3, can be seen to have remarkable properties with regard to BOD removal for both domestic wastewater and river water. The removal efficiency was over 80% for all tested water, except for S3 in Mzingazi river water, where it was just 79%.

4. Materials and Methods

4.1. Synthesis of Iron@Copper Core–Shell Nanoparticles

The synthesis of core–shell nanoparticles was achieved using the description by Yu et al. [16], where 10 mL of 0.02 M FeCl_3 aqueous solution was prepared in a flask, after which 0.5 g of biofloculant was added. A 10 mL aliquot of 5.0 M NaOH was added to the solution of FeCl_3 at room temperature. This mixture was added into a 10 mL solution of glucose (1.0 M). A color change indicated the formation of iron nanoparticles. To obtain different ratios of iron to copper, different volumes were prepared. The first ratio of 1:3 was prepared by mixing 25 mL (0.003 M) FeCl_3 with 75 mL (0.003 M) of CuCl_2 and the 1:1 ratio was achieved by mixing 50 mL of each sample as indicated; consequently, the final 3:1 ratio was obtained by mixing 75 mL (0.003 M) of FeCl_3 and 25 mL (0.003 M) of CuCl_2 . All different ratios were prepared and added into 0.5 g of purified biofloculant. The reaction was allowed to continue for 20 min and the resulting precipitate was collected through centrifugation at 15 000 rpm, 4 °C, for 30 min [16].

4.2. Test for Flocculation Activity of S1, S2, and S3

Flocculation activity was evaluated using a method developed by Kurane et al. [17] with a slight modification, where 4 g of kaolin clay was dissolved in a liter of distilled water. One hundred milliliters of the prepared kaolin solution was mixed with 2 mL of nanoparticle solution at a concentration of 2 mg/mL and 3 mL of CaCl_2 (1 g/L) solution was also added, after which the mixture was shaken for a minute and transferred to a 100 mL graduated measuring cylinder. To observe the flocculation ability of the synthesized core–shell nanoparticles the mixture was left to stand for 5 min at room temperature and only the upper part was employed for analysis using a Pharo 100 Spectrophotometer® (Capital Lab Supplies CC, Durban, South Africa) [17]. Flocculation activity was calculated according to the equation

$$\text{Flocculation activity (FA)\%} = \frac{A - B}{A} \times 100 \quad (1)$$

where A is the optical density of the control at 550 nm and B is the optical density of the sample at 550 nm.

4.3. Optimization of S1, S2, and S3 in Flocculation Activity

Optimization of core–shell nanoparticles was achieved by varying various parameters such as dosage, temperature, pH, and cations against a kaolin clay solution. To evaluate the dosage effect 0.2–0.8 mg/mL concentrations were prepared. The dosage that resulted in the highest flocculation activity was used for subsequent experiments. Trivalent, divalent, and monovalent cations were evaluated for their effect on flocculation activity. Thermostability of the material was verified by varying the temperature (60, 80, and 100 °C). Finally, evaluation of the effect of pH was conducted by changing the pH to 3, 7, and 11, which represented acidic, neutral, and alkaline conditions, respectively.

All these parameters were varied in order to establish conditions that favored the optimal flocculation activity [18].

4.4. Dye Removal by Core-Shell Nanoparticles

Dyes such as safranin, methylene blue, methylene orange, and malachite green were used to evaluate the removal efficiency of core-shell nanoparticles. Core-shell nanoparticles of 0.2 mg were dissolved in 50 mL distilled water, after which 2 mL of nanoparticle solution was mixed with dye solution (4 g/L) and the mixture shaken for a minute and allowed to stand at room temperature for 5 min. Each dye solution was measured at a maximum wavelength and all the experiments were conducted in triplicate. The supernatant was analyzed using a Pharo 100 Spectrophotometer®. The following formula was used for calculating the removal efficiency (RE), i.e.,

$$RE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i is the initial value before addition of nanoparticles and C_f is the value after the treatment with core-shell nanoparticles.

4.5. Characterization of S1, S2, and S3

4.5.1. Morphological Studies and Elemental Analysis of S1, S2, and S3

A scanning electron microscope JEOL JSM 6100 SEM with Bruker Quantax Esprit software (JEOL USA, Inc., Peabody, Massachusetts 01960, USA) equipped with EDX techniques was used for the morphological and compositional information of the samples S1, S2, and S3. SEM images were taken using a tungsten (W) filament operated at an emission current and accelerator voltage of 100 μ A and 10 kV, respectively. SEM samples were prepared by placing a small quantity of the material on double-sided carbon tape stuck on a copper stub and coated with carbon (JEOL USA, Inc., Peabody, MA 01960, USA) [19].

4.5.2. FT-IR and X-Ray Diffraction Analysis of S1, S2, and S3

FT-IR spectroscopy was used to identify and confirm the functional groups present in the biofloculants using a Bruker Tensor 27 FT-IR spectrometer (Bruker, Gauteng, South Africa). FT-IR spectra were recorded for the dry powder samples with a resolution of 4 cm^{-1} in the range 4000–200 cm^{-1} .

The crystallinity of the synthesized samples was studied using a Bruker D8 Advance diffractometer (Bruker, Johannesburg, South Africa) equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 40 mA at room temperature. The dry samples were placed on a sample holder and the diffraction patterns were recorded from 5° to 90°.

4.5.3. Thermogravimetric Analysis of S1, S2, and S3

Thermogravimetric analysis was performed on the synthesized samples using a Perkin-Elmer Thermal Analysis Pyris 6 TGA (PerkinElmer, Inc., Waltham, MA 02451, USA). High temperatures ranging 22° to 900 °C were used to heat the biofloculants at a constant rate of ramping of 10 °C min^{-1} and under a constant flow of nitrogen gas [20].

4.6. Statistical Analysis

The experimental data was collected in triplicate and error bars in the figures represent the standard deviation of the data. All data were subjected to one-way variance analysis using graph pad prism version 6.1, where a significant level of $p < 0.05$ was used.

5. Conclusions

In this work, characterization of biofloculant synthesized Fe@Cu core-shell nanoparticles was achieved by the use of Fourier-transform infrared spectroscopy, X-ray diffractometry, and scanning electron microscopy. The FTIR analysis revealed the presence of hydroxyl, amine, and amide groups in the samples. XRD analysis showed deep peaks at $2\theta \sim 35^\circ$, 40° , and 65° in S1. Contrary to this, it was noted that the strongest peaks were at $2\theta \sim 35^\circ$, 45° , 65° , and 77° for S2. In S3, the strongest peaks were observed at $2\theta \sim 22^\circ$ and 30° , and morphological studies revealed an amorphous-like structure for all three samples. When evaluated for flocculation activity the synthesized samples (S1, S2, and S3) were effective at a low dosage concentration of 2 mg/mL, were thermostable, and could flocculate at all pH. Cations are not necessary in the flocculation process while using these samples. All three samples revealed some remarkable properties for dye removal as the removal efficiency was above 89% for all dyes tested. The synthesized Fe@Cu core-shell nanoparticles could remove nutrients such as total nitrogen and phosphate in both domestic wastewater and Mzingazi river water. Furthermore, high removal efficiencies for COD and BOD were also observed, with S3 being the most effective sample, followed by S2, and S1 being the least effective.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/7/755/s1>, Figure S1: UV spectra of Fe@Cu core-shell nanoparticles, Figure S2: TEM images of Fe@Cu core-shell nanoparticles, Figure S3: TGA analysis of samples (a) S1 (b) S2 and (c) S3.

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