Applications and biosafety of the Fe@Cu core-shell nanoparticles

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A broad range of applications and interesting properties of core-shell nanoparticles (CSNs) such as catalysis, sensors, material chemistry, biology, and water purification have gained the huge interest of most researchers in recent years. The aim of the study was to synthesise Fe@Cu CSNs nanoparticles using a bioflocculant and to evaluate its potential application in flocculation activity (FA), wastewater treatment, and as an antimicrobial agent. A dosage of 0.2 mg/mL Fe@Cu CSNs was found to be the most effective with 99% FA and also has an advantage to flocculate at a wider pH range of 3–11 (acidic, neutral and alkaline). Thermostability of the engineered nanomaterials (ENMs) was evaluated between the temperatures range of 60–100 °C, however, 96% FA was retained, indicating the thermal stability of the ENMs. The addition of cation, Ca^{2+}, further improved the flocculation activity to the highest reading of 99%. The high removal efficiency (RE) of chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen and phosphate was observed in all wastewater samples examined. The removal efficiency of the dyes was found to be above 93% for all dye samples. The ENMs possess antimicrobial activity against both Gram-positive and Gram-negative microorganisms. The Minimal Inhibitory Concentration (MIC) and Bactericidal Minimal Concentration (MBC) were observed at a lower concentration of 1.563 mg/mL. Cell viability against HEK293 and MCF7 was high at the lower concentration; with the increase in concentration the decrease in cell viability was observed.

Keywords: application, Fe@Cu core-shell, nanoparticles, removal efficiency, synthesis

Toepassings en bioveiligheid van Fe@Cu kern-in-dop nanodeeltjies: Die afgelope paar jaar is daar groot belangstelling by navorsers vir die verskeidenheid toepassings en interessante eienskappe van kern-in-dop (Eng. Core-shell) nanodeeltjies (CSN's) in toegepaste velde soos katalise, sensors, materiaalchemie, biologie en watersuiwering. Ons resultate dui aan dat CSN's in 'n dosis van 0.2 mg/mL die doeltreffendste is vir flokkulasie in afvalwater met 'n flokkulasie-aktiwiteit (FA) van 99% oor 'n wye pH-reeks van 3-11 (suur, neutraal en alkalies). Die termostabiliteit van die vervaardigde nanomateriale (ENM's) is tussen 60-100 °C in toepassings getoets waar daar nog steeds 'n 96% flokkulasie-aktiwiteit, bevestigend van die termiese stabiliteit van die ENM's, gevind is. Die toevoeging van 'n katioon soos Ca^{2+}, het die flokkulasie-aktiwiteit tot 99% verbeter. Die hoë verwyderingsdoeltreffendheid (RE) van COD, BOD, totale stikstof en fosfate is waargeneem in alle afvalwater wat ondersoek is. Die RE van kleurstowwe is groter as 93% vir alle kleurstofmonsters wat ge-evalueer is vir flokkulasie. Die ENM's het antimikrobiese aktiwiteit teen beide Gram-positiewe en Gram-negatiewe mikroorganismes getoon. Die minimum inhiberende konsentrasie (MIC) en die minimum bakteridodende konsentrasie (MBC) is waargeneem teen 'n lae vlak van 1.563 mg/mL. Sellewensvatbaarheidstudies teenoor HEK293 en MCF7 selle was effektief by lae konsentrasies, asook gedurende 'n toename in konsentrasie van ENM's.

Sleutelwoorde: Toepassing, Fe@Cu kern-in-dop, nanodeeltjies, verwyderingsdoeltreffendheid, sintese.

Introduction

A crucial aspect of our life is water, the essential feature of our planet. The oceans hold about 97% of our water and only 1% of fresh water is accessible for use (Corcoran, 2010). The world has been facing a crisis of both the quality and quantity of water since the beginning of the 21st century. This is due to industrialisation, ever increasing populations, food production practices, etc. Both liquid and solid waste is produced in every community and this waste reaches our water bodies. Wastewater contains nutrients which stimulate the growth of aquatic life and may also contain compounds which are toxic, i.e. mutagenic or carcinogenic compounds (Tchobanoglous et al., 1991).

The major water pollutants are colloids and are mostly kinetically unstable, which makes them hard to remove, as they do not settle under gravity (Santschi, 2018). The removal of colloids presents an enormous challenge due to electrokinetic properties on their surface (Bampole and Bafubiandi, 2018). A physicochemical technique, which is often used to enhance flocs to form larger flocs that can be removed through sedimentation, floatation or filtration, is called flocculation (Abdullah et al., 2017). In the last decade synthetic and chemical flocculants have been used in wastewater treatment due to their high efficacy (Okaiyeto et al., 2016). However, synthetic and chemical flocculants such as polyacrylamide derivatives and aluminum sulfate have high efficiency, but are reported to be detrimental to both the environment and humans (Guo and Yu, 2014).

Material at nanoscale size with cores (inner material) and shells (outer material) are traditionally defined as core-shell nanoparticles (CSNs) (Wang et al., 2013). Because of their remarkable properties and application in diverse areas including catalysis, nanomaterial has attracted vast attention in the recent past (Galperin and Margel, 2007, Sondi and Salopek-Sondi, 2004, Li et al., 2018, Kefeni et al., 2018, Dlamini et al., 2020). Furthermore, researchers have, over the past few decades, viewed conventional heterogeneous catalysts from a new perspective as the result of rapid nanotechnology development (Gawande et al., 2015). As a result, nanoparticles (NPs) have been found to possess excellent properties for their application in the treatment of wastewater (Dlamini et al., 2019b, Tiwari et al., 2008).

The present paper aims to investigate the efficacy of iron copper ENMs in the treatment of wastewater and river water. For this purpose, the removal efficacy of pollutants such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), phosphate and total nitrogen was examined. Furthermore, this study seeks to establish the biosafety of ENMs synthesised using bioflocculant.

Material and methods

Bioflocculant extraction and purification

The source of a bioflocculant was the bacteria that was previously isolated from the marine environment of Sodwana Bay, KwaZulu-Natal province of South Africa, and was identified as *Alcaligenes faecalis* using nucleotide sequencing of the 16S rRNA. The bacterial strains were stored at -80 ℃ for preservation. The bioflocculant production medium was prepared according to the method given by Dlamini et al. (2019b). This consisted of glucose (20 g), $MgSO_4 \cdot 7H_2O$ (0.2 g), $(NH_4)_2SO_4$ (0.2 g), K_2HPO_4 (5 g), urea (0.5 g), yeast extract (0.5 g) and KH_2PO_4 (2 g) in a litre of filtered seawater at pH 8. Bioflocculant was extracted and purified, the culture medium was inoculated with the *A. faecalis* HCB2 and incubated for 3 days at 30 ℃ with a shaking speed of 160 revolutions per minute (rpm). The mixture was centrifuged at 5000 rpm, 4 ℃, for 30 min, the supernatant was collected and subjected into 2000 mL ethanol for extraction and allowed to precipitate at 4 ℃ for 12 h. The precipitate was vacuum dried, the crude bioflocculant that was obtained was dissolved in 100 mL of distilled water, and a mixture of 79 mL chloroform, 21 mL butanol was added and left for 12 h at room temperature to allow sedimentation of pure bioflocculant which was finally collected and vacuum dried.

Synthesis of ENMs

To synthesise both iron and copper NPs a series of steps was followed as described by Dlamini et al. (2019a). A solution of both copper sulphate ($CuSO_4$) and iron sulphate ($FeSO_4$) was used. 3.0 mM of each solution was prepared separately and was added to 0.5 g of pure bioflocculant in a conical flask. The mixtures were allowed to stand at room temperate overnight. The control was the bioflocculant solution excluding the copper sulphate and iron sulphate. The synthesised NPs were collected by centrifuge at 4000 rpm for 15 min at 4 °C (Dlamini et al., 2019b).

To synthesise ENMs a similar method with minor modifications, as described by Yu et al. (2017), was followed. 3.0 mM solutions of $CuSO_4$ with different volumes of 10, 20, 30 mL were sequentially added to iron nanoparticles (FeNPs). The reaction was allowed to continue for 20 min after which the precipitate was harvested by centrifuge at 15000 rpm at 4 °C for 30 min.

Characterisation of ENMs

BRUKER D8 Advance Diffractometer operated at 40 kV, 40 mA, with graphite monochromatised CuKα1 radiation of wavelength λ = 1.5406 Å was used to investigate the phase composition and crystallinity of core-shell nanoparticles. The diffraction pattern of the nanoparticles was recorded in the 2θ range from 20° to 80° at scanning steps of 0.03°. A sample of 0.1 mL was taken and diluted with 2 mL of deionised water to investigate UV–Vis spectrum of nanoparticles, as a function of reaction time using a Perkin-Elmer spectrophotometer in the 300 to 700 nm wavelength region operated at a resolution of 1 nm. Field emission scanning electron microscopy (FESEM) (JSM-6700, JEOL, Japan) was used to examine synthesised NPs. The synthesised NPs were mounted on specimen stubs with

double-sided adhesive tape coated with gold in a sputter coater. A drop of aqueous solution containing the nano-particles was placed on carboncoated copper grids and dried under an infrared lamp (JEM 2010, JEOL, Japan) (accelerating voltage – 200.0 kV). Energy dispersive X-ray analysis (EDXA) combined with FESEM was used to ascertain the composition of the NPs synthesised.

Evaluation of flocculation activity of ENMs

Kaolin clay (4 g/L) was used as the suspend solute for experimentation. 100 mL of kaolin solution was mixed with 1% of 3 mL $CaCl_2$ and 2 mL of 0.2 mg/mL of ENMs. The mixture was then transferred to a 250 mL conical flask and was shaken in the shaking incubator for 1 min at 165 rpm, after which the mixture was transferred to a graduated measuring cylinder and allowed to stand for 5 min. The supernatant liquid was analysed using a spectrophotometer at 550 nm. Flocculation activity (FA) was calculated using the equation below:

$$FA\ (\%) = \frac{[A - B]}{A} X\ 100 \qquad (1)$$

Where: A and B are the optical density of both the sample and the control at 550 nm.

Determination of physico-chemical parameters in wastewater samples

The wastewater samples were collected aseptically using autoclaved scotch bottles, preserved in ice, and were assessed promptly once they got into the lab. The sample sites are all located in KwaZulu-Natal, South Africa. The sampling sites are Mzingazi River, Vulindlela water treatment plant and Tendele coal mine wastewater. The characteristic properties of each water sample before treatment was found as: Mzingazi River (pH 7.3, absorbance 2.8, COD 3.300 mg/L, BOD 136 mg/L, total nitrogen 0.223 mg/L and phosphate 85.7 mg/L); Vulindlela wastewater (pH 6.4, absorbance 2.8, total nitrogen 13.1 mg/L and phosphate 3.38 mg/L); and Tendele coal mine wastewater (pH 7.3, absorbance 2.9, COD 842 mg/L and BOD 123.2 mg/L).

Application of ENMs in dye removal and wastewater treatment

To evaluate the RE of NPs in the water samples, test kits (COD, BOD, phosphate and total nitrogen) were used in accordance with manufacturer protocol and all the residuals were analysed in a UV-Vis spectrophotometer Pharo 300 Spectroquant® at 680 nm. For RE of dyes, different samples of dyes were prepared by dissolving (4 g/L) in distilled water, after which 100 mL of dye solution was mixed with 2 mL of 0.2 mg/mL of ENMs. The mixture was then transferred to a 250 mL conical flask and was shaken vigorously in the shaking incubator at room temperature for 1 min at 165 rpm. Thereafter the mixture was transferred to a graduated measuring cylinder and was allowed to stand for 10 min. The supernatant liquid was analysed using a spectrophotometer at the maximum

wavelength for each dye (Dlamini et al., 2019b). The RE was calculated using the following equation:

$$RE\ (\%) = \frac{C0 - C1}{C0} X\ 100 \qquad (2)$$

Where: C0 is the initial value and C1 is the value after the flocculation treatment with ENMs.

Antimicrobial activity of ENMs

Bacillus subtilis CSM5 and *Escherichia coli* ATCC 25922 (1.0 mL) were used to evaluate the antimicrobial ability of ENMs. Firstly, both strains were resuscitated by inoculation into the freshly prepared and autoclaved nutrient broth and then incubated overnight at 37 °C. The absorbance of the organisms was then adjusted using spectrophotometer at 600 nm according to McFarlan standard (0.5). To determine both the Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC), the 96-microplate-well method was adopted and cipro-floxacin 40% and distilled water were used as a positive and negative control respectively. Firstly, all wells were flooded with 50 µL of sterile nutrient broth, followed by the addition of 50 µL inoculum of *Bacillus subtilis* and *Escherichia coli*. Subsequently 50 µL of ENMs with 0.2 mg/mL was added in the first rows of 96 well micro plates and followed by a series of dilutions from the highest concentration to the lowest to ensure that all wells had 50 µL remaining. *P-iodonitrotetrazolium* (INT) was used as an indicator (Eloff, 1998). Mueller Hinton agar was used to evaluate the MBC where the wells, which did not indicate color, were streaked on a sterile agar and incubated at 37 °C for 12 h. The lowest concentration of nanoparticles that exhibited the complete killing of the trial organisms was considered as the MBC.

In-vitro cytotoxicity of ENMs

The description according to Daniels and Singh (2019) was followed to achieve in-vitro cytotoxicity of ENMs. Cell lines HEK293 and MCF7 were used to ascertain the cytotoxicity of the ENMs. To plate the cells with cell suspensions of 1×10^5 cells/mL concentrations, 96-well plates were employed. Using the tenfold dilution method, cells were seeded with different concentrations of 25–100 µg/µL of nanoparticles after 48 hours of incubation. To administrate the nanoparticles, a medium containing 1% foetal bovine serum (FBS) was used and the plates were incubated for 48 hours. Cell viability was ascertained with the use of tetrazolium salt (Sigma) as an indicator. 15 µL of MTT (5 mg/mL) in phosphate-buffered saline (PBS) was added to each well and incubated at 37 °C for 4 h. The medium containing MTT and formed formazan crystals was dissolved in 100 µL of dimethyl sulfoxide (DMSO) after sucking off the wells, after which a microplate reader was used to read the solution. Iits optical density was measured at 570 nm. The following formula was used to determine cell viability:

Cell viability
$$(\%) = \frac{F1}{F0} X\ 100$$

Where F1 and F0 are the final values obtained after and before treatment with the nanoparticles, respectively.

Software and statistical analysis

All the experimentation was conducted in triplicate and the error bars in the Figures show the standard deviations of the data. Data were subjected to one-way analysis of variance using Graph Pad PrismTM 6.1. P values ≤ 0.05 were regarded as significant. Values with different letter of the alphabet along the same row are significantly different ($p < 0.05$).

Results

Characterisation of ENMs

Characterisation of the NPs was done in our previous work and it included Fourier transform-infrared spectroscopy (FT-IR), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) (Dlamini et al., 2020).

The dosage effect on the flocculation activity of ENMs

Figure 1 represents the results obtained during the evaluation of ENM's effect of dosage concentration on the flocculation activity. The highest flocculation activity of above 90% was observed for all the dosage concentrations.

Effect of cation presence in flocculation process

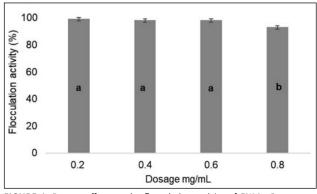Table 1 shows the results for the presence of cations and their effect on flocculation activity. The ENMs flocculate well in the absence of cations with the flocculation activity above 90%.

The effect of pH on the flocculation activity of ENMs

The results displayed in Figure 2 show the effect of pH on the flocculation process. The optimum pH was 7 with 99% flocculation activity.

Thermostability of ENMs

Figure 3 denotes the findings of the effect of heat on the flocculation of ENMs. The results indicate that the nanoparticles are thermostable as the flocculation activity was above 90% at 100 °C.

Application of ENMs on dye removal

Figure 4 represents the results of dye removal by ENMs. The as-synthesised nanoparticles shows the removal efficiency of above 90% for all dyes. With 95% as the highest for malachite green, safranin and methylene orange dyes and the lowest removal with 93% for methylene blue.

TABLE 1: Effect of cations on the flocculation activity of ENMs.

Cations	Flocculation Activity (%) ± SD
Control	95 ± 0.3[a]
Fe^{3+}	97 ± 0.0[a]
Ca^{2+}	99 ± 0.2[a]
Na^+	97 ± 0.2[a]

Values represent mean ± deviation of replicate readings.

FIGURE 1: Dosage effect on the flocculation activity of ENMs. Percentage flocculating activities with different letters (a & b) are significantly ($p < 0.05$) different.
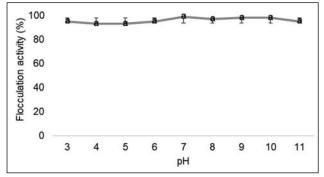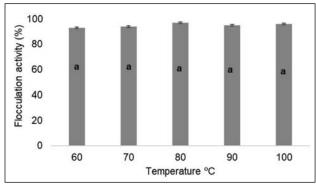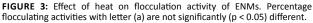

FIGURE 2: Effect of pH on flocculation activity of ENMs. Percentage flocculating activities with letter (a) are not significantly ($p < 0.05$) different.

FIGURE 3: Effect of heat on flocculation activity of ENMs. Percentage flocculating activities with letter (a) are not significantly ($p < 0.05$) different.
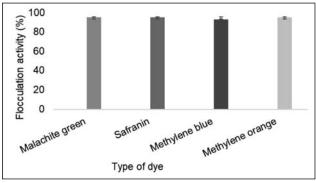

FIGURE 4: Removal of dyes by ENMs.

In-vitro cytotoxicity test of ENMs on HEK 293 and MCF7

Table 2 shows the results of Minimal Inhibitory Concentration (MIC) and Minimal Bactericidal Concentration (MBC) of the nanoparticles. The ENMs have the MIC and MCB for both the Gram-positive and Gram-negative microorganisms.

Discussion

A flocculant with a high efficacy at the lowest dosage concentration is a necessity in wastewater treatment. From Figure 1, ENMs revealed some interesting capabilities when tested against kaolin clay as the flocculation activity was observed to be highest at 0.2 mg/mL with 99% flocculation activity. With the increase in dosage, a slight decrease in flocculation activity between 0.4–0.6 mg/mL was observed, and the lowest flocculation activity was observed at the highest concentration of 0.8 mg/mL. Further increase in dosage concentration is likely to result in limited floc formation due to excess flocculant competing for binding sites (Guibai and Gregory, 1991). From Figure 1 it can be deduced that the ENMs are commercially viable as they are effective at lowest concentration.

The presence of cation is significant in a flocculation process. The cation neutralises the charge of both the kaolin
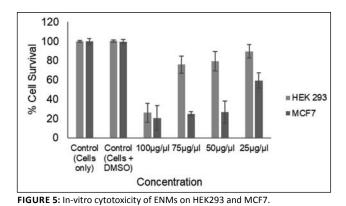

FIGURE 5: In-vitro cytotoxicity of ENMs on HEK293 and MCF7.

TABLE 2: The antimicrobial effect of ENMs.

Antimicrobial agent	Bacterial strain	MIC (mg/mL)	MBC (mg/mL)
Fe@Cu Core-shell	*E. coli*	1.563	1.563
	B. subtilis	1.563	1.563
Ciprofloxacin	*E. coli*	12.5	12.5
	B. subtilis	6.25	6.25

suspension and the flocculant, which in turn facilitate the formation of flocs (Manivasagan et al., 2015). In Table 1, all the evaluated cations, i.e. trivalent, divalent and monovalent, facilitated the flocculation process with the Ca^{2+} having the highest reading at 99%. However, the ENMs could flocculate well even in the absence of cations as the control had 95% flocculation activity. As shown in Table 1, the statistical significance of the flocculation activity was not that noteworthy, as indicated in parenthesis. This makes the ENMs a possible alternative to some chemical flocculants which have been found to be neurotoxic, carcinogenic and environmentally unfriendly (Shevah, 2016). Similar results have been documented in a study conducted by Dlamini et al. (2019b), where it was demonstrated that copper nanoparticles contributed a flocculation activity up to 96% in the absence of cation.

The ENMs are pH stable and are suitable for application both in acidic and alkaline wastewater. From Figure 2 it is evident that the flocculation activity of ENMs fluctuated at pH 3 with flocculation activity of 95%. Slight change in pH (between 4–6) resulted in constant flocculation activity of 93% as can be observed, and at neutral pH 7 the optimum activity of 99% was witnessed. These current findings suggest that the ENMs have potential applications in both acid mine wastewater and alkaline water. The ability of ENMs to withstand extreme acidic and alkaline conditions is also shown.

Thermostability of nanoparticles was assessed, where the ENMs were exposed in a water bath for 30 min at different temperatures (Figure 4). The flocculation activity was above 90% at all the temperatures with 80 ℃ having the highest flocculation activity of 97%. Thermostability of the ENMs can be attributed to the temperature-resistant nature of the bioflocculant that is polysaccharide in nature, from which the ENMs were synthesised (Maliehe et al., 2019). Moreover, both iron and copper have a high boiling point which may also contribute to the heat-resistant nature of the ENMs. Furthermore, composite/core-shell material is said to be able to withstand extremely high temperatures (Yu and Dutta, 2011).

Textile industries are one of the main sources producing huge amounts of effluent, which end up reaching water bodies when untreated. Most pigmenting material used during processing are not only toxic to the environment

TABLE 3: Wastewater treatment using ENMs.

Flocculant	Type of wastewater	Pollutant type	Water quality before treatment (mg/mL)	Water quality after treatment (mg/mL)	Removal efficiency (%)
ENMs	Coal mine water	COD	842	71	92
		BOD	123.2	3.1413	97
	Mzingazi River water	COD	3.300	0.793	76
		BOD	136	70	94
		Phosphate	85.7	0.109	99
		Total nitrogen	0.223	0.014	94
	Domestic wastewater	Phosphate	3.38	0.127	97
		Total nitrogen	13.1	2.096	84

(Buthelezi et al. (2012)), but also are not degradable (Verma, 2008). The released textile wastewater causes adverse effects to the environment due to its toxicity, pigmentation and non-degradability. Moreover, the ecosystem is disturbed by these colouring agents from textile effluents, as the light cannot penetrate through the aquatic plants for photosynthesis (Merzouk et al., 2010). The highest dye removal efficiency of 95% was observed in malachite green, safranin and methylene orange. The lowest dye removal efficiency of 93% was detected for methylene blue.

MTT assay was used to investigate the cytotoxicity of ENMs on MCF7 and HEK293 cell lines (Moodley and Singh, 2019). From Figure 5 it can be seen that the cell viability of normal cells (HEK293) is 89% at 25 µg/µL and with the increase in concentration of the ENMs, the viability decreased to 75% at 75 µg/µL, which indicates that the nanoparticles are safer to use. However, at the highest concentration (100 µg/µL) the cell viability was below 50%, which suggests that at higher concentration the ENMs are not safe. Contrary to this, the ENMs were found to be toxic against cancerous cells (MCF7) as the viability was below 50% at the second lowest concentration of 50 µg/µL.

Antimicrobial activity of ENMs was assessed against Gram-positive and Gram-negative microorganisms. Here 40% ciprofloxacin was used as a positive control while 0.2 mg/mL of ENMs was present. The ENMs proved to be more effective as both the MIC and MBC were achieved at low concentration of 1.563 mg/mL for both E. coli and B. subtilus. Contrary to this, when ciprofloxacin was used, the results revealed that the MIC and MBC for *E. coli* and *B. subtilus* are 12.5 and 6.25 mg/mL respectively.

For easy disposal of waste and convenient water access, most industries are situated along riverbanks. A wide range of contaminants such as heavy metals, hydrocarbons, alkalis, chlorinated hydrocarbons and other chemicals often greatly change the water pH (Lokhande et al., 2011). There are high concentrations of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the coal mine wastewater as shown in Table 3 and the ENMs were able to remove up to 92% and 97% respectively. In Mzingazi River water, the high concentration of BOD can be attributed to crop and animal waste, and industrial effluent discharge as there are farms and industries near the Mzingazi River. The ENMs removed up to 95% of BOD while COD removal efficiency was 76%. Total nitrogen and phosphate removal for domestic wastewater was 84% and 97% respectively, while total nitrogen and phosphate removal efficacy for Mzingazi river water was 94% and 99%.

Conclusion

The ENMs are effective to flocculate at a low concentration of 0.2 mg/mL, cation independent, pH stable and thermostable. The ENMs possess antimicrobial effect for both Gram-positive and Gram-negative microorganisms and the MIC and MBC, found at the lowest concentration

of 1.563 mg/mL are found to be non toxic against normal cells at low concentration. Remarkable properties to remove dyes (at a concentration of 4 g/L) with just 0.2 mg/mL dosage size were revealed. High removal efficacy of contaminants in wastewater and river water was also observed. Production of ENMs using bioflocculants holds a great potential in terms of application, as the technique is not complex and not harmful to the environment as there are no harmful chemicals used during production. For possible application in the future, it is recommended that more characterisation be done on the ENMs and the mechanism of action should be evaluated.

Conflicts of Interest

The authors declare that there is no conflict of interest.

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