Article

Magnetic Field Effect on Coagulation Treatment of Wastewater Using Magnetite Rice Starch and Aluminium Sulfate

Nomthandazo Precious Sibiya *, Gloria Amo-Duodu, Emmanuel Kweinor Tetteh and Sudesh Rathilal

Green Engineering Research Group, Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Durban University of Technology, Durban 4001, South Africa
* Correspondence: nomtha.presh@gmail.com

Abstract: The use of synthetic coagulants to reduce suspended particles from drinkable water and wastewater is prompting new issues because it poses many health and environmental risks. Hence, improving the coagulation process using sophisticated nanotechnology with a magnetic field (MF) for quick recoverability emerges as being useful. In this study, the effects of magnetite rice starch (MS) and aluminum sulfate (alum) were investigated at a constant dose (3 g or 3000 mg/L) using a Jar test (six beakers) as potential low-cost coagulants for industrial wastewater treatment. At a high magnification of $1000\times$ and a surface pore size of 298 μm, scanning electron microscopy and energy dispersive X-ray (SEM/EDX) analyses were utilized to elucidate the morphology of the coagulants. Coagulation was performed at 150 rpm (quick mixing) for 2 min, and 30 rpm (slow mixing) for 15 min. Thereafter, samples were allowed to settle (10–60 min) with and without MF. The findings showed more than 65% contaminants removal (turbidity and TSS) and 30% chemical oxygen demand (COD) removal using alum while MS showed 80% contaminants removal (turbidity and TSS) and 50% COD removal. MS showed an increase of more than 3% in contaminants removal (COD, turbidity, and TSS) when exposed to MF. As a result, the use of MS together with MF in water and wastewater treatment is anticipated as an environmentally benign and effective coagulant.

Keywords: coagulation; magnetite; rice starch; magnetized coagulant; alum

1. Introduction

Rapid industrialization has brought several environmental problems as a result of wastewater produced from various industrial activities. Depending on the industry, wastewater may contain a variety of contaminants such as lactose, oils and greases, proteins, nitrogen, and phosphorus-rich compounds, sediments, other organic materials, and detergents [1–5]. When this wastewater is released into the ecosystem without adequate treatment, it poses a severe ecological concern with significant health and environmental consequences [1,6,7]. As a result, adequate treatment is essential to improve the ultimate quality of the effluent before final disposal [8,9]. The existing wastewater treatment system outlines the methods such as primary treatment (separation of suspended solids and large solid objects via screening), secondary treatment (reduction of dissolved solids and organic matter via basic activated sludge, coagulation, disinfection, and so on), and tertiary treatment (additional process to further remove nutrients) [2,8,10–12]. To achieve severe water quality regulations, coagulation has been often utilized to improve the quality of treated wastewater [1,13]. Coagulation/flocculation (CF) involves many stages, including the electrostatic interaction between negatively charged suspended impurities and cationic proteins, followed by particle destabilization [3,4,14–17]. Coagulants derived from chemicals such as $(Al_2(SO_4)_3$ (alum), lime, and $FeCl_3$ are often used in conventional CF processes due to their accessibility of use and low cost [18]. Nevertheless, the chemical-based coagulants were ruled inappropriate owing to the potential dangers and disastrous consequences on marine organisms [7,14,19–24]. Furthermore, they change the pH of the water, which might

cause secondary pollution [25,26].The remaining aluminium particles in treated water have been connected to Alzheimer's disease. [27–30]. Due to the drawbacks of these coagulants, there has been a quest for eco-friendly and sustainable coagulants for their usage. Natural coagulants are available locally, generate less sludge, and produce biodegradable sludge (which may be reused). They can also be waste-based resources such as fruit wastes, eggshells, cassava peel, okra leaves, and so on. [1,31]. In its unprocessed form, starch is one of the world's most common natural polymers, composed of the polymers amylose and amylopectin, which are two anhydroglucose unit polymers [32,33]. Amylose is a non-branching helical polymer composed of $-1,4$ linked D-glucose monomers, whereas amylopectin is a polymer with several branches made up of $-1,4$ and $-1,6$ connected D-glucose monomers [34,35]. Due to its recyclability, biocompatibility, and low cost, starch has received commercial interest as a coagulant [32,34].

The advancement of nanotechnology has significantly aided in the development of novel approaches to numerous health and environmental challenges while using less energy [36,37]. Numerous research have been undertaken to establish magnetite's efficacy: Fe_3O_4 (F) in the reduction of harmful metals and dangerous compounds from water and demonstrate the effectiveness of this material [38–43]. Fe_3O_4 can be used to coat a variety of surfactants to reduce aggregates induced by atomic magnetic interactions between molecules [44,45]. In terms of application, it has unique and favorable characteristics: cheap expense and danger, high magnetic, durability, bio-compatibility, and simplicity of dissociation from aqueous solution [44,46,47]. The fact that it is super paramagnetic, suggests that it responds to a magnet, making sample and collection easier and faster [48]. However, as the external magnetic field is removed, its magnetization diminishes. The employment of MF enhances settling capacities, decreasing the concentration of suspended particles and activated sludge, and boosting the wastewater management efficacy [49]. Previous research has demonstrated the efficacy of natural coagulants (rice starch, okra, eggshell, cassava leaves, banana peels, chitosan, moringa oleifera, etc.) via treating of turbidity through the neutralization of negatively-charged particles with positively-charged polymers [2,24,50–53]. Therefore, this study aims to efficiently investigate alum and rice starch incorporated with magnetite (MS) in wastewater treatment with and without MF. Lastly, scanning electron microscopy and energy dispersive X-ray (SEM/EDX) were utilized to investigate the elemental composition and the morphology of the coagulants under investigation.

2. Materials and Methods

2.1. Material

All of the reagents employed in the research were analytical graded and did not require additional purification, except for the stated ones and the deionized water (ELGA WATERLAB, PURELAB Option-Q water deionizer (High Wycombe, London, UK)) utilized in the stock solutions' preparation. The chemicals utilized comprised NaOH pellets, $FeSO_4.7H_2O$, oleic acid (surfactant), ethanol, alum ($Al_2(SO_4)_3$), $FeCl_3.6H_2O$, and the rest of reagents utilized in the preparation of synthetic wastewater were analytical grade and supplied by Sigma Aldrich (Kempton Park, South Africa). Rice starch was acquired from a local market (Shoprite, Durban, South Africa), washed with distilled water, and then oven dried for 24 h at 80 °C.

2.2. Synthetic Wastewater

At room temperature, the synthetic wastewater was made-up by mixing peptone (4 g), glucose (2.75 g), $NaHCO_3$ (27.5 g), urea (0.75 g), meat extract (6.25 g), $MgSO_4.7H_2O$ (0.05 g), K_2HPO_4 (0.7 g), $CuCl_2.2H_2O$ (0.00125 g), NaCl (0.22 g), and $CaCl_2$ (0.10 g) in 20 L of deionized water and 5 L of wastewater taken from a local wastewater treatment plant after chlorination process in eThekwini municipal area of South Africa [35]. The synthetic wastewater was evaluated for turbidity, TSS, and COD immediately after preparation, by APHA [54]. Turbidity was measured using a turbidimeter (Hach, 2100N (Loveland,

Colorado)) while COD and TSS were measured using a spectrophotometer (HACH, DR 3900 (Düsseldorf, Germany)). The synthetic wastewater sample (0.2 mL) was measured, placed in the COD high range vials (HACH), and digested at 150 °C for 2 h. Following digestion, the bottles were cooled to 25 °C before the COD was measured using the spectrophotometer indicated above. The initial synthetic wastewater concentrations were measured in terms of turbidity (82.50 ± 1.105 NTU), COD (351.80 ± 0.781 mg/L), and total suspended solids (TSS; 77.33 ± 1.697 mg/L). While the received wastewater had an initial turbidity of 11.78 NTU, 6.5 mg/L TSS and 73 mg/L COD.

2.3. Synthesis of Magnetite Rice Starch (MS)

Firstly, the stock solutions of 0.4 M Fe^{3+} and 0.2 M Fe^{2+} were made by weighing 108.12 g and 55.61 g, respectively, and dissolving them in 1 L deionized water. In addition, a 3 M NaOH stock solution was prepared by dissolving 199.99 g of NaOH in 1 L of deionized water [35,55]. The magnetite (F) was then synthesized in a volume ratio of 1:1 by utilizing 500 mL of each of the Fe^{3+} and Fe^{2+} stock solutions. To achieve homogeneity, the solution was constantly agitated on a magnetic hotplate then 4 mL of oleic acid was added drop-wise. The pH of the solution was then adjusted to 12 with 250 mL of 3 M NaOH until a black precipitate appeared. The thick black precipitate was then heated (aged) at 70 °C. To remove any undesirable particles, the supernatant was decanted, and the precipitate was washed three times with distilled water and ethanol which was then oven drying at 80 °C for 12 h. After properly combining 20 g rice starch and 20 g magnetite (F), the magnetic rice starch (MS) was calcined in a Kiln Furnace (Cape Town, South Africa) at 550 °C for 1 h. The physical morphologies and elemental compositions of the coagulants (rice starch, alum, magnetite, and MS) were investigated at the University of Cape Town, South Africa, using scanning electron microscopy and energy dispersive X-ray (SEM/EDX) equipment (Nova NanoSEM paired with EDT and TLD detector).

2.4. Coagulation

Coagulation tests were performed at 25 ± 3 °C in beakers containing 500 mL of wastewater using a jar-test (VELP Scientifica, JTL6, Usmate Velate MB, Italy) as indicated in Figure 1. Each beaker was dosed with 3 g of coagulant at a contact pH (7.2) measured using Hanna pH-meter (Hanna Instruments, HI98130 (Durban, South Africa)). The impact of the settling period (10–60 min) with and without magnetics Field (MF) on pollutants elimination (turbidity, TSS, and COD) was also investigated. The beakers were then stirred swirled for 2 min at a fast-mixing rate of 150 rpm, followed by 15 min of flocculation at 30 rpm for 15 min [30,31] before being allowed to settle. The proportion of contaminants (COD, turbidity, and TSS) was determined using the Equation (1).

$$E_{removal}(\%) = \frac{B_A - B_B}{B_A} \times 100 \tag{1}$$

where B_A and B_B represent the initial and final values of each pollutant (TSS or turbidity or COD), and E is the % removal.

Figure 1. A jar test (JTL6) set-up for the coagulation/flocculation process.

3. Results and Discussion

3.1. Scanning Electron Micrograph (SEM)/Energy Disperse X-Ray (EDX)

The magnetite, alum, rice starch, and MS were measured at a micro-scale of 100 μm, with a magnification of 1000×, a horizontal field width of 298 μm, and a landing energy capacity of 20 keV (Figure 2). Figure 2a–d depicts the SEM findings of alum, magnetite, rice starch, and MS obtained at working distances (WD) of 6.2, 6.1, 5.5 and 5.2 mm, respectively, ranging from large to low porosity, which may be owing to the high calcination temperature of 550 °C, which improved the wastewater adsorption capacity [36,55]. Alum (Figure 2a) image shows irregular-shaped particles in the middle of the surface produced by the agglomerations of various sizes of crystals. There are no obvious surface fractures, indicating that calcination did not generate dehydration [56]. Rice starch particles may be distinguished by particle size and granule shape [57,58].

Figure 2b demonstrated a smooth and solid surface with holes. The images of rice starch from this study coincide with the findings of Saritha et al. [58]. The crystallinity to carbohydrates might not have had a significant impact on water clarification efficacy. However, the characteristics of gluing that are related to crystalline phase level may have a good results on the removal of turbidity [59,60]. The magnetite (Figure 2c) exhibited a regular cellular structure that is similar to previous research [36,55]. Figure 2d shows an extreme filmed surface, at which MS revealed clusters with many pores. Furthermore, magnetizing rice starch had little influence on its shape since no depression, fractures, or hollow granules were found.

Figure 3 shows the EDX micrograms of the coagulants studied. The magnetite spectra (Figure 3a) revealed an O (40.04%) > C (32%) > Fe (27.96%) composition, whereas the alum spectrum (Figure 3b) revealed an O (57.72%) > S (20.96%) > C (11.53%) > Al (9.79%) composition similar to previous study [36], and composition of C (84.55%) > O (14.62%) > p (0.43%) > K (0.40%) was found in spectra of rice starch (Figure 3c). The strong appearance of C & O peaks confirms the hypothesis that the rice starch granules are entirely composed of carbohydrate monomers [61,62]. Literature shows that magnetite is made up primarily of iron and oxygen [39,41,55,63]. Significant proportions of new components of S (5.54%), Cl (6.44%), and Fe (23.34%) were also discovered. MS spectrum (Figure 3d) reveals Fe binding energies at 0.6, 6.4, and 7 keV. Furthermore, the content of oxygen increased from 14.62 to 34.44%, whereas carbon content reduced from 84.55 to 30.24%. This confirms the effective synthesis of magnetized rice starch, which has improved the possibility of antibacterial and metal binding properties in various regions of the coagulant.
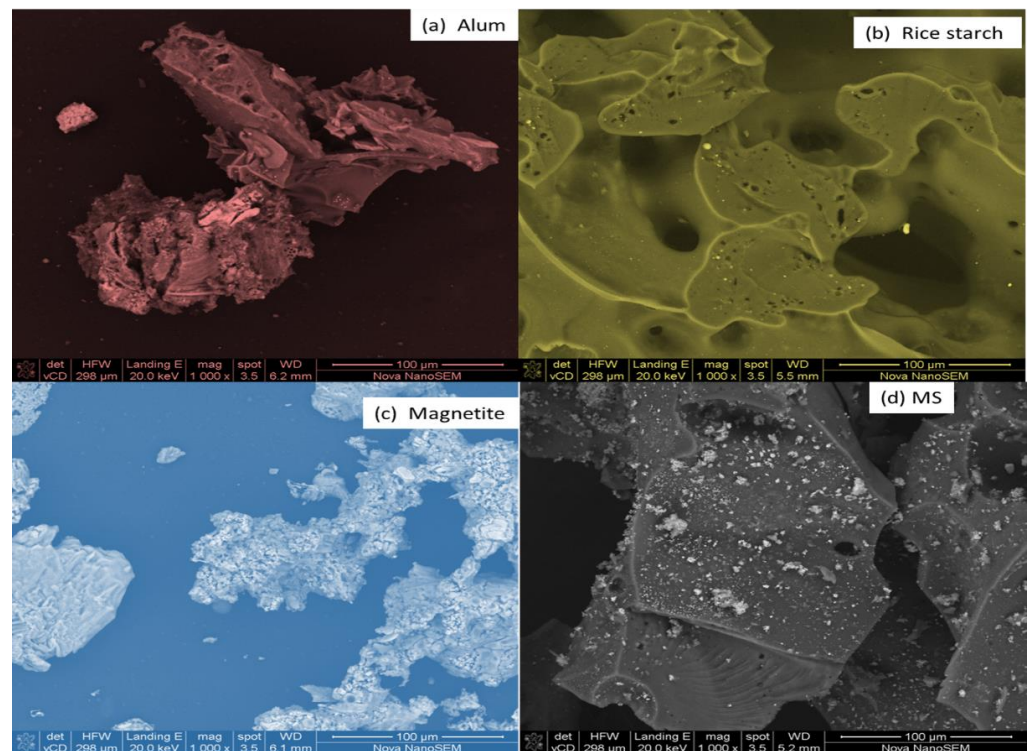
Figure 2. SEM images of coagulants before coagulation taken at a view field of 298 μm at a high magnification of 1000×; (**a**) alum, (**b**) rice starch, (**c**) magnetite, and (**d**) MS.
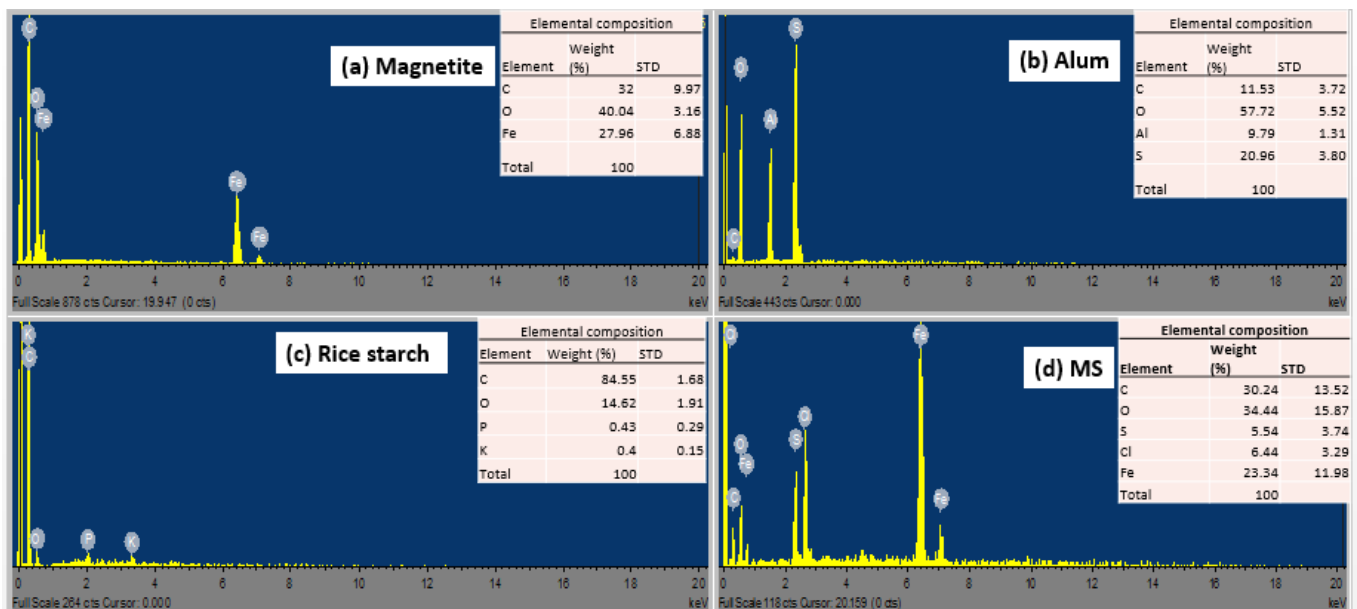

Figure 3. EDX images of (**a**) magnetite, (**b**) alum, (**c**) rice starch, and (**d**) MS.

3.2. Comparative Study of Magnetic Effect Using MS and Alum

Figure 4 depicts the results of alum and MS treatments with and without MF (20 mT) over constant 60 min settling phase. Figure 4a shows that when a magnetic field was applied during the settling phase, turbidity, TSS, and COD efficiency increased from 84.78 to 87.57%, 83.55 to 86.03%, and 49.94 to 51.93%, respectively. The presence of magnetite in rice starch and MF led to higher treatability efficiencies and settle ability of the agglomerated flocs, and lower energy use [64,65]. The positively charged magnetite aided the

adsorption of negatively charged pollutants in the wastewater sample [48], whereas the cationic exchange mechanism (electrostatic, van der Waals, and chemical bonding) and the generation of hydroxide on the surface of MS was used to reduce contaminants by magnetic measures [18,37,66]. Finally, amylase and amylopectin in rice starch destabilize colloidal particles by bridging and agglomeration [18,67,68]. As shown in Figure 4b, there is no significant/observable change in the use of the alum, when the magnetic field was applied. This might be due to lack of paramagnetic properties of the alum; whereas the magnetic entity of the MS (Figure 4a) facilitated its aggregation and settleability when the magnetic field was applied.
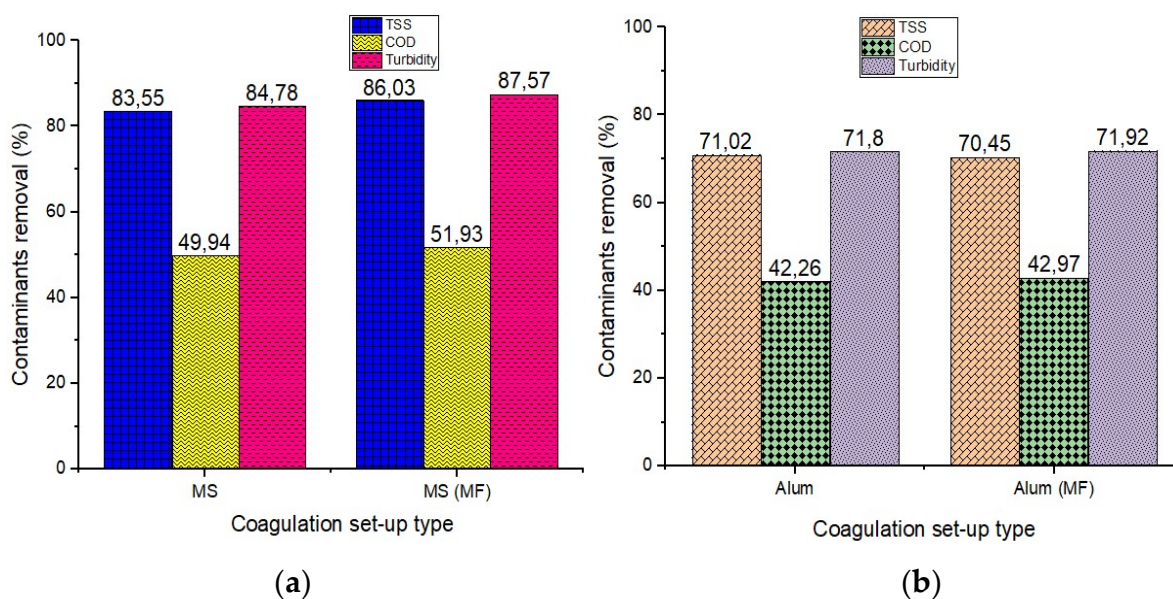

(**a**)　　　　　　　　　　　　　　　　　　　(**b**)

Figure 4. Effect of magnetic field using (**a**) MS and (**b**) alum on contaminants removal (%).

It was observed that there is an intermolecular relationship between turbidity and TSS elimination (Figure 5) since they display a similar pattern [36,69]. Findings show that MS eliminated turbidity and TSS by more than 80% in both settling configurations, whereas alum eliminated turbidity and TSS by more than 70%. With settling durations ranging from 10 to 30 min, alum was found to enhance colloidal aggregation and destabilization (as demonstrated in the treatment of organic material and hydrophilic organic matter) for all contaminants (TSS, turbidity, and COD).

Colloidal stability and destabilization are produced by an enhancement in ionic strength with a slight decrease in zeta potential and a decrease in the thickness of the diffuse half of the electrical double layer [36,70–73]. Following that, the treatment ability of contamination (TSS and turbidity) became unstable. Since additional pollutants have been adsorbed, the flocs' settling capacity has decreased as a result of a colloidal breakdown in suspension [37,74]. Due to general interaction between oxygen-containing groups (hydroxyl and carboxyl) and negatively charged colloidal particles, the surfaces may have become more hydrophilic (less hydrophobic) [36,75–78]. Figure 5c demonstrates that alum (>30 min) efficiency decreased at 40 min and then rose till the 60th min. The dramatic decrease in contaminants removal with time (30–40 min) for alum reflects the fact that the number of particles accessible for coagulation decreased as the reaction continued. This might be because of the flocs mechanism or the combination bridging mechanism [36,79]. Figure 5 suggests that extending the settling time improves removal performance for MS and MS (MF) until 40 min, at which point effectiveness begins to decline until 60 min. The residual contaminants decrease between 10 and 40 min resulting in the formation of large-size flocs with a greater settling velocity [80,81], but the trend almost reverses between 50 and 60 min, which could be due to colloidal entrapment and high attractive force dominants [12,36,75]. Although 40 min produced higher efficiencies, 30 min was

chosen due to the quick and reasonable responses. As a result, the shorter the duration of settling, the more effective the procedure in terms of sludge reduction or management. The removal efficiency results for turbidity, TSS, and COD were recorded for each coagulant at an optimum settling time of 30 min (Alum: 74.03%, 73.80%, and 45.03%; MS: 86.25%, 85.09%, and 55.04%; and MS (MF): 87.95%, 88.24% and 55,97%). Table 1 shows different types of magnetized coagulants utilized in the treatment of various wastewaters.
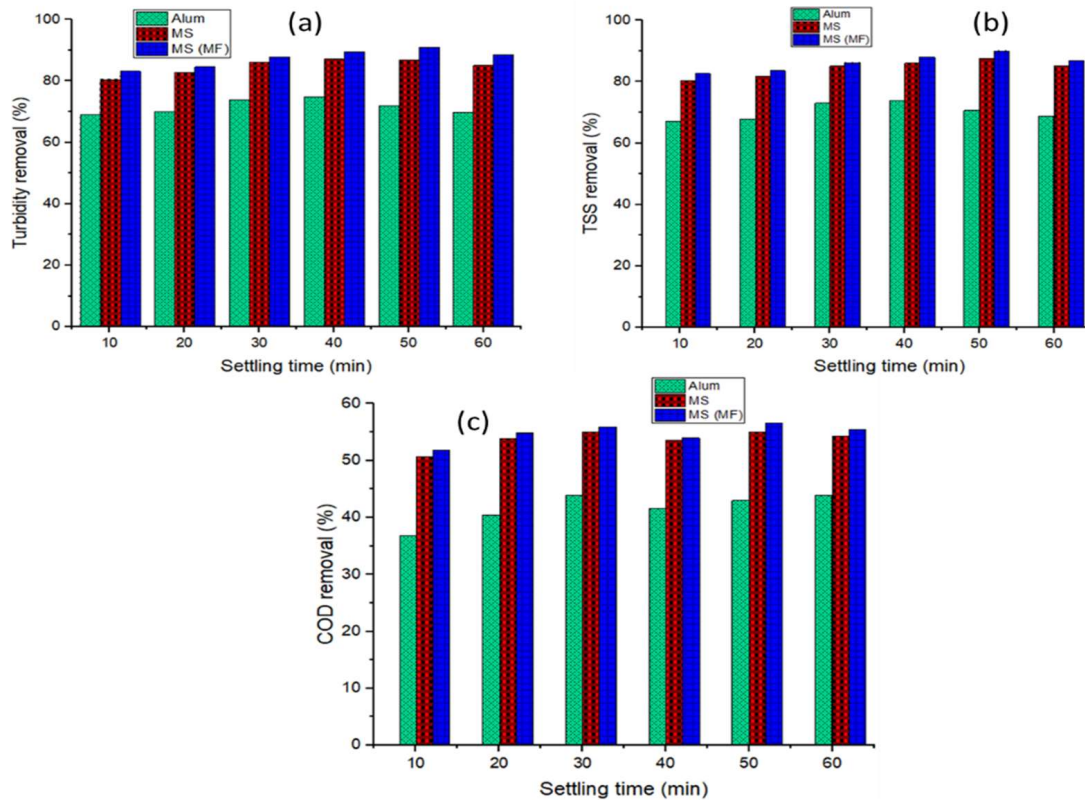

Figure 5. Results on (**a**) turbidity, (**b**) TSS, and (**c**) COD removal (%) with the effect of settling time.

Table 1. Different types of magnetized coagulants are used in the treatment of wastewaters.

Type of Coagulant/(s)	Effluent Source/(s)	Optimum Conditions	Contaminant Removal Efficiency	Reference/(s)
Magnetized eggshell	Synthetic wastewater	20 mg/L dosage 30 min settling	94.86% TSS 92.56% turbidity	[36]
Magnetized moringa oliferea	Surface raw water	400 mg/L dosage 30 min settling time	94.4% turbidity	[43]
	Textile wastewater	30 mg/L dosage 10 min magnetic exposure	91.43% turbidity	[46]
	Sanitation wastewater	10 mg/L dosage 30 min magnetic exposure	90% turbidity	[50]
Magnetized alum	Synthetic wastewater	20 mg/L dosage 30 min settling	99.75% TSS 99.50% turbidity	[36]
Magnetite rice starch (MS)	eThekwini municipal synthetic wastewater	3000 mg/L dosage, 30 min settling time	86.25% turbidity, 85.09% TSS, and 55.04% COD	This study
Magnetite rice starch (MS)	eThekwini municipal synthetic wastewater	3000 mg/L dosage 30 min magnetic exposure	87.95% turbidity, 88.24% TSS and 55.97% COD	This study
Magnetized alum	Textile effluent	50 mg/L 50 min magnetic exposure	85% turbidity	[37]

4. Conclusions

Rice starch magnetite (MS) was produced utilizing a co-precipitation approach that combined rice starch with Fe_3O_4 in a 1:1 ratio. Analytical data obtained using scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray (EDX) spectroscopy confirmed the success of MS surface morphology and elemental compositions. The presence of multivalent ions (Fe, P, K, S, Cl Al) and their associated carbonates was verified by SEM/EDX, indicating a successful synthesis. The influence of settling time was explored in this research using alum and magnetite rice starch (MS) with and without exposure to a magnetic field (MF). At a settling period of 30 min with and without MF, the treatability performance of MS demonstrated more than 80% removal efficiency (turbidity and TSS) and more than 49% elimination of COD. MS (MF) has demonstrated a strong potential for water and wastewater treatment as an alternative to traditional alum. The addition of magnetite to rice starch resulted in faster particle aggregation and greater flocs size, this made quick settling possible. This finding implies that incorporating a magnetic field and magnetite rice starch into the coagulation process is a viable potential for wastewater treatment.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gautam, S.; Saini, G. Use of natural coagulants for industrial wastewater treatment. *Glob. J. Environ. Sci. Manag.* **2020**, *6*, 553–578.
2. Nimesha, S.; Hewawasam, C.; Jayasanka, D.; Murakami, Y.; Araki, N.; Maharjan, N. Effectiveness of natural coagulants in water and wastewater treatment. *Glob. J. Environ. Sci. Manag.* **2021**, *8*, 101–116.
3. Nath, A.; Mishra, A.; Pande, P.P. A review natural polymeric coagulants in wastewater treatment. *Mater. Today Proc.* **2020**, *46*, 6113–6117. [CrossRef]
4. Nharingo, T.; Zivurawa, M.T.; Guyo, U. Exploring the use of cactus opuntia ficus indica in the biocoagulation–flocculation of Pb(II) ions from wastewaters. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 3791–3802. [CrossRef]
5. Aboelfetoh, E.F.; Aboubaraka, A.E.; Ebeid, E.-Z.M. Binary coagulation system (graphene oxide/chitosan) for polluted surface water treatment. *J. Environ. Manag.* **2021**, *288*, 112481. [CrossRef] [PubMed]
6. Tetteh, E.K.; Rathilal, S.; Chetty, M.; Kwaku Armah, E.; Asante-Sackey, D. Treatment of Water and Wastewater for Reuse and Energy Generation-Emerging Technologies. In *Water and Wastewater Treatment*; IntechOpen: London, UK, 2019. [CrossRef]
7. Noor, M.H.M.; Lee, W.J.; Azli, M.F.Z.i.M.; Ngadi, N.; Mohamed, M. Moringa oleifera extract as green coagulant for POME Treatment: Preliminary studies and sludge evaluation. *Mater. Today Proc.* **2021**, *46*, 1940–1947. [CrossRef]
8. Kurniawan, S.B.; Abdullah, S.R.S.; Imron, M.F.; Said, N.S.M.; Ismail, N.I.; Hasan, H.A.; Othman, A.R.; Purwanti, I.F. Challenges and opportunities of biocoagulant/bioflocculant application for drinking water and wastewater treatment and its potential for sludge recovery. *Int. J. Environ. Res. Public Health* **2020**, *17*, 9312. [CrossRef]
9. Ahmed, S.N.; Ali, S.J.; Ali, A.H.; Mohammed, A. Improvement of organic matter removal in water produced of oilfields using low cost Moringa peels as a new green environmental adsorbent. *Glob. Nest* **2020**, *22*, 268–274.

10. Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. *Environ. Chem. Lett.* **2018**, *17*, 145–155. [CrossRef]

11. Nizamuddin, S.; Siddiqui, M.; Mubarak, N.; Baloch, H.A.; Abdullah, E.; Mazari, S.A.; Griffin, G.; Srinivasan, M.; Tanksale, A. Iron oxide nanomaterials for the removal of heavy metals and dyes from wastewater. In *Nanoscale Materials in Water Purification*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 447–472.

12. Zhang, H.; Lin, H.; Li, Q.; Cheng, C.; Shen, H.; Zhang, Z.; Zhang, Z.; Wang, H. Removal of refractory organics in wastewater by coagulation/flocculation with green chlorine-free coagulants. *Sci. Total Environ.* **2021**, *787*, 147654. [CrossRef]

13. Kumar, P.A.; Pathak, S.; Singh, A.; Khanduri, H.; Wang, X.; Basheed, G.A.; Pant, R.P. Optimization of cobalt concentration for improved magnetic characteristics and stability of CoxFe3-xO4 mixed ferrite nanomagnetic fluids. *Mater. Chem. Phys.* **2021**, *265*, 124476. [CrossRef]

14. Nnaji, N.J.N.; Ani, J.U.; Aneke, L.E.; Onukwuli, O.D.; Okoro, U.C.; Ume, J.I. Modelling the coag-flocculation kinetics of cashew nut testa tannins in an industrial effluent. *J. Ind. Eng. Chem.* **2014**, *20*, 1930–1935. [CrossRef]

15. Kumar, M.M.; Karthikeyan, R.; Anbalagan, K.; Bhanushali, M.N. Coagulation process for tannery industry effluent treatment using Moringa oleifera seeds protein: Kinetic study, pH effect on floc characteristics and design of a thickener unit. *Sep. Sci. Technol.* **2016**, *51*, 2028–2037. [CrossRef]

16. Tetteh, E.K. Optimisation of Dissolved Air Flotation (DAF) for Separating Industrial Mineral Oil from Water. Ph.D. Thesis, Department of Chemical Engineering, Durban University of Technology Durban, Durban, South Africa, 2018. Available online: https://openscholar.dut.ac.za/bitstream/10321/3182/1/TETTECHEK_2018.pdf (accessed on 25 March 2021).

17. Cui, H.; Huang, X.; Yu, Z.; Ping Chen, P.; Cao, X. Application progress of enhanced coagulation in water treatment. *RSC Adv.* **2020**, *10*, 20231. [CrossRef]

18. Sibiya, N.; Amo-Duodu, G.; Tetteh, E.K.; Rathilal, S. Response surface optimisation of a magnetic coagulation process for wastewater treatment via Box-Behnken. *Mater. Today: Proc.* **2022**, *62*, S122–S126. Available online: https://www.sciencedirect.com/science/article/pii/S221478532200671X (accessed on 7 August 2022). [CrossRef]

19. Ndabigengesere, A.; Narasiah, K.S. Use of Moringa oleifera seeds as a primary coagulant in wastewater treatment. *Environ. Technol.* **2010**, *19*, 789–800. [CrossRef]

20. Varsha, M.; Kumar, P.S.; Rathi, B.S. A review on recent trends in the removal of emerging contaminants from aquatic environment using low-cost adsorbents. *Chemosphere* **2022**, *287*, 132270. [CrossRef]

21. Ahmed, J.; Thakur, A.; Goyal, A. Chapter 1:Industrial Wastewater and Its Toxic Effects. In *Biological Treatment of Industrial Wastewater*; Royal Society of Chemistry: London, UK, 2021; pp. 1–4.

22. Mogbo, O.N.; Iorwua, M.B.; Duweni, E.C.; Tiza, M.T. A study on the efficacy of bio-coagulants for turbid and waste water treatment. *J. Crit. Rev.* **2020**, *7*, 1307–1315.

23. Kakoi, B.; Kaluli, J.W.; Ndiba, P.; Thiong'o, G. Banana pith as a natural coagulant for polluted river water. *Ecol. Eng.* **2016**, *95*, 699–705. [CrossRef]

24. Lim, I.; Lee, E.; Park, H.-U.; Jang, J.; Jung, N.; Yang, T.-H.; Yim, S.-D.; Park, G.-G. Sonochemical gram-scale synthesis of core–shell PdCo@ Pt nanoparticle and investigation of post heat-treatment effect for various gas atmospheres. *J. Alloys Compd.* **2021**, *879*, 160441. [CrossRef]

25. Ahmed, S.I.; Heiba, Z.K.; Ibrahim, M.M.; Shaltout, A.A.; Alzahrani, E.; Wahba, H.H.; Alsubaie, M.F. Synthesis and Characterization of Eco-Friendly CMC/Maghemite Nanocomposite Films. *J. Electron. Mater.* **2021**, *50*, 7098–7109. [CrossRef]

26. Chollom, M.N.; Rathilal, S.; Swalaha, F.M.; Bakare, B.; Tetteh, E.K. Anaerobic treatment of slaughterhouse wastewater: Evaluating operating conditions. *WIT Trans. Ecol. Environ.* **2019**, *239*, 251–262. Available online: https://www.witpress.com/elibrary/wit-transactions-on-ecology-and-the-environment/239/37478 (accessed on 3 May 2022).

27. Muniza, G.L.; Borges, A.C.; da Silva, T.C.F.; Batista, R.O.; de Castro, S.R. Chemically enhanced primary treatment of dairy wastewater using chitosan obtained from shrimp wastes: Optimization using a Doehlert matrix design. *Environ. Technol.* **2020**, *43*, 237–254. [CrossRef] [PubMed]

28. Mosaddeghi, M.R.; Pajoum Shariati, F.; Vaziri Yazdi, S.A.; Nabi Bidhendi, G. Application of response surface methodology (RSM) for optimizing coagulation process of paper recycling wastewater using Ocimum basilicum. *Environ. Technol.* **2020**, *41*, 100–108. [CrossRef] [PubMed]

29. Oke, E.O.; Araromi, D.O.; Jimoda, L.A.; Adetayo Adeniran, J. Kinetics and neuro-fuzzy soft computing modelling of river turbid water coag-flocculation using mango (Mangifera indica) kernel coagulant. *Chem. Eng. Commun.* **2019**, *206*, 254–267. [CrossRef]

30. Asharuddin, S.M.; Othman, N.; Altowayti, W.A.H.; Bakar, N.A.; Hassan, A. Recent advancement in starch modification and its application as water treatment agent. *Environ. Technol. Innov.* **2021**, *23*, 101637. [CrossRef]

31. Chua, S.-C.; Chong, F.-K.; Yen, C.-H.; Ho, Y.-C. Valorization of conventional rice starch in drinking water treatment and optimization using response surface methodology (RSM). *Chem. Eng. Commun.* **2021**, *208*, 613–623. [CrossRef]

32. Kumar, V.; Al-Gheethi, A.; Asharuddin, S.M.; Othman, N. Potential of cassava peels as a sustainable coagulant aid for institutional wastewater treatment: Characterisation, optimisation and techno-economic analysis. *Chem. Eng. J.* **2021**, *420*, 127642. [CrossRef]

33. Hamidi, D.; Fard, M.B.; Yetilmezsoy, K.; Alavi, J.; Zarei, H. Application of Orchis mascula tuber starch as a natural coagulant for oily-saline wastewater treatment: Modeling and optimization by multivariate adaptive regression splines method and response surface methodology. *J. Environ. Chem. Eng.* **2021**, *9*, 104745. [CrossRef]

34. Sibiya, N.P.; Amo-Duodu, G.; Tetteh, E.K.; Rathilal, S. Model prediction of coagulation by magnetised rice starch for wastewater treatment using response surface methodology (RSM) with artificial neural network (ANN). *Sci. Afr.* **2022**, *17*, e01282. Available online: https://www.sciencedirect.com/science/article/pii/S2468227622001892 (accessed on 16 August 2022). [CrossRef]

35. Sibiya, N.P.; Rathilal, S.; Tetteh, E.K. Coagulation Treatment of Wastewater: Kinetics and Natural Coagulant Evaluation. *Molecules* **2021**, *26*, 698. [CrossRef] [PubMed]

36. Tetteh, E.K.; Rathilal, S. Application of magnetized nanomaterial for textile effluent remediation using response surface methodology. *Mater. Today Proc.* **2020**, *38*, 700–711. Available online: https://www.sciencedirect.com/science/article/pii/S2214785320326341 (accessed on 17 September 2021). [CrossRef]

37. Li, X.; Wang, C.; Zhang, J.; Liu, J.; Liu, B.; Chen, G. Preparation and application of magnetic biochar in water treatment: A critical review. *Sci. Total Environ.* **2020**, *711*, 134847. [CrossRef]

38. Samrot, A.V.; Sahithya, C.S.; Selvarani, J.; Purayil, S.K.; Ponnaiah, P. A review on synthesis, characterization and potential biological applications of superparamagnetic iron oxide nanoparticles. *Curr. Res. Green Sustain. Chem.* **2021**, *4*, 100042. [CrossRef]

39. Ramimoghadam, D.; Bagheri, S.; Abd Hamid, S.B. Progress in electrochemical synthesis of magnetic iron oxide nanoparticles. *J. Magn. Magn. Mater.* **2014**, *368*, 207–229. [CrossRef]

40. Petcharoen, K.; Sirivat, A. Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. *Mater. Sci. Eng. B* **2012**, *177*, 421–427. [CrossRef]

41. Chua, S.-C.; Ho, Y.-C.; Chong, F.-K. Synthesis and application of a novel composite coagulant aid from rice starch and sesbania seed gum for water treatment. *Malays. J. Chem.* **2021**, *23*, 7–14.

42. dos Santos, T.R.T.; Silva, M.F.; de Andrade, M.B.; Vieira, M.F.; Bergamasco, R. Magnetic coagulant based on Moringa oleifera seeds extract and super paramagnetic nanoparticles: Optimization of operational conditions and reuse evaluation. *Desalination Water Treat.* **2018**, *106*, 226–237. [CrossRef]

43. Dung, D.T.K.; Hai, T.H.; Phuc, L.H.; Long, B.D.; Vinh, L.K.; Truc, P.N. Preparation and characterization of magnetic nanoparticles with chitosan coating. *J. Phys. Conf. Ser.* **2009**, *187*, 012036. [CrossRef]

44. Akbarzadeh, A.; Samiei, M.; Davaran, S. Magnetic nanoparticles: Preparation, physical properties, and applications in biomedicine. *Nanoscale Res. Lett.* **2012**, *7*, 144. [CrossRef]

45. dos Santos, T.R.T.; Mateus, G.A.P.; Silva, M.F.; Miyashiro, C.S.; Nishi, L.; de Andrade, M.B.; Fagundes-Klen, M.R.; Gomes, R.G.; Bergamasco, R. Evaluation of Magnetic Coagulant (α-Fe$_2$O$_3$-MO) and its Reuse in Textile Wastewater Treatment. *Water Air Soil Pollut.* **2018**, *229*, 92. [CrossRef]

46. Wang, Y.; Li, B.; Zhou, Y.; Jia, D. Chitosan-induced synthesis of magnetite nanoparticles via iron ions assembly. *Polym. Adv. Technol.* **2008**, *19*, 1256–1261. [CrossRef]

47. Saifuddin, N.; Dinara, S. Pretreatment of palm oil mill effluent (POME) using magnetic chitosan. *E-J. Chem.* **2011**, *8*, S67–S78. [CrossRef]

48. Haritwal, A.; Mohan, D.; Chaudhary, M.; Asopa, P.P.; Modi, G. Study on the improved biogas generation through magnetic field modified anaerobic digestion. *Int. J. Eng. Res. Technol.* **2015**, *4*, 1175–1179.

49. Santos, T.R.; Silva, M.F.; Nishi, L.; Vieira, A.M.; Fagundes-Klen, M.R.; Andrade, M.B.; Vieira, M.F.; Bergamasco, R. Development of a magnetic coagulant based on Moringa oleifera seed extract for water treatment. *Environ. Sci. Pollut. Res.* **2016**, *23*, 7692–7700. [CrossRef]

50. Amran, A.H.; Zaidi, N.S.; Muda, K.; Loan, L.W. Effectiveness of natural coagulant in coagulation process: A review. *Int. J. Environ. Sci. Technol.* **2018**, *7*, 34–37.

51. Jagaba, A.H.; Kutty, S.R.M.; Hayder, G.; Latiff, A.A.A.; Aziz, N.A.A.; Umaru, I.; Ghaleb, A.A.S.; Abubakar, S.; Lawal, I.M.; Nasara, M.A. Sustainable use of natural and chemical coagulants for contaminants removal from palm oil mill effluent: A comparative analysis. *Ain Shams Eng. J.* **2020**, *11*, 11951–11960. [CrossRef]

52. Ang, W.L.; Mohammad, A.W. State of the art and sustainability of natural coagulants in water and wastewater treatment. *J. Clean. Prod.* **2020**, *262*, 121267. [CrossRef]

53. APHA. *Standard Methods for the Examination of Water and Wastewater*; APHA: Washington, DC, USA, 2012; Available online: https://www.standardmethods.org/doi/book/10.2105/SMWW.2882?gclid=CjwKCAiA25v_BRBNEiwAZb4-ZRdKz6ceq6 (accessed on 23 June 2020).

54. Amo-Duodu, G.; Tetteh, E.K.; Rathilal, S.; Armar, E.K.; Adedeji, J.; Chollom, M.N.; Chetty, M. Effect of engineered biomaterials and magnetite on wastewater treatment: Biogas and kinetic evaluation. *Polymers* **2021**, *13*, 4323. [CrossRef]

55. Duong, L.V.; Wood, B.J.; Kloprogge, J.T. XPS study of basic aluminum sulphate and basic aluminium nitrate. *Mater. Lett.* **2005**, *59*, 1932–1936. [CrossRef]

56. Higgins, P.D.R.; Skup, M.; Mulani, P.M.; Lin, J.; Chao, J. Increased Risk of Venous Thromboembolic Events With Corticosteroid vs Biologic Therapy for Inflammatory Bowel Disease. *Clin. Gastroenterol. Hepatol.* **2015**, *13*, 316–321. [CrossRef] [PubMed]

57. Saritha, V.; Karnena, M.K.; Dwarapureddi, B.K. "Exploring natural coagulants as impending alternatives towards sustainable water clarification"—A comparative studies of natural coagulants with alum. *J. Water Process Eng.* **2019**, *32*, 100982. [CrossRef]

58. Ruan, Y.; Zhang, K.; Wu, C.; Wu, R.; Lam, P.K.S. A preliminary screening of HBCD enantiomers transported by microplastics in wastewater treatment plants. *Sci. Total Environ.* **2019**, *674*, 171–178. [CrossRef] [PubMed]

59. Serajuddin, M.; Chowdhury, M.A.; Haque, M.M.; Haque, M.E. Using Turbidity to Determine Total Suspended Solids in an Urban Stream: A Case Study. *Int. J. Eng. Trends Technol. (IJETT)* **2019**, *67*, 84–88.

60. Asharuddin, S.M.; Othman, N.; Zin, N.S.M.; Tajarudin, H.A.; Din, M.F. Flocculation and antibacterial performance of dual coagulant system of modified cassava peel starch and alum. *J. Water Process Eng.* **2019**, *31*, 100888. [CrossRef]

61. Asharuddin, S.M.; Othman, N.; Zin, N.S.M.; Din, M.F.M.; Kumar, V. Synthesis and Characterization of Dual Properties Coagulant from Natural Precursors for Raw Water Treatment. *Int. J. Integr. Eng.* **2020**, *12*, 257–267. [CrossRef]

62. Talekar, S.; Joshi, A.; Kambale, S.; Jadhav, S.; Nadar, S.; Ladole, M. A tri-enzyme magnetic nanobiocatalyst with one pot starch hydrolytic activity. *Chem. Eng. J.* **2017**, *325*, 80–90. [CrossRef]

63. Ambashta, R.D.; Sillanpaa, M. Water purification using magnetic assistance: A review. *J. Hazard. Mater.* **2010**, *180*, 38–49. [CrossRef]

64. Zhang, Y.; Wu, B.; Xu, H.; Liu, H.; Wang, M.; He, Y.; Pan, B. Nanomaterials-enabled water and wastewater treatment. *NanoImpact* **2016**, *3–4*, 22–399. [CrossRef]

65. Hatamie, A.; Parham, H.; Zargar, B.; Heidari, Z. Evaluating magnetic nano-ferrofluid as a novel coagulant for surface water treatment. *J. Mol. Liq.* **2016**, *219*, 694–702. [CrossRef]

66. Teh, C.Y. Potential use of rice starch in coagulation–flocculation process of agro-industrial wastewater: Treatment performance and flocs characterization. *Ecol. Eng.* **2014**, *71*, 509–519. [CrossRef]

67. Bratby, J. *Coagulation and Flocculation in Water and Wastewater Treatment*, 3rd ed.; IWA Publishing: London, UK, 2016.

68. Mateus, G.A.P.; dos Santos, T.R.T.; Sanches, I.S.; Silva, M.F.; de Andrade, M.B.; Paludo, M.P.; Gomes, R.G.; Bergamasco, R. Evaluation of a magnetic coagulant based on Fe3O4 nanoparticles and Moringa oleifera extract on tartrazine removal: Coagulation-adsorption and kinetics studies. *Environ. Technol.* **2018**, *41*, 1–16. [CrossRef] [PubMed]

69. Duan, J.; Gregory, J. Coagulation by hydrolysing metal salts. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 475–502. [CrossRef]

70. Maiga, D.T.; Nyoni, H.; Nkambule, T.T.; Mamba, B.B.; Msagati, T.A.M. Impact of zinc oxide nanoparticles in aqueous environments: Influence of concentrations, natural organic matter and ionic strength. *Inorg. Nano-Met. Chem.* **2020**, *50*, 680–692. [CrossRef]

71. Matusiak, J.; Grządka, E.; Bastrzyk, A. Removal of hazardous oxide nanoparticles by the biopolymer flocculation in the presence of divalent salt. *Chem. Eng. J.* **2021**, *423*, 130264. [CrossRef]

72. Rakshit, A.K.; Naskar, B.; Moulik, S.P. Stability of hydrophobic colloids: Perspectives and current opinion. *J. Dispers. Sci. Technol.* **2021**, *42*, 503–513. [CrossRef]

73. Daud, Z.; Awang, H.; Latif, A.A.A.; Nasir, N. Suspended solid, color, COD and oil and grease removal from biodiesel wastewater by coagulation and flocculation processes. *Procedia Soc. Behav. Sci.* **2015**, *195*, 2407–2411. [CrossRef]

74. Zhao, Y.; Gao, B.; Shon, H.; Cao, B.; Kim, J.-H. Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts. *J. Hazard. Mater.* **2011**, *185*, 1536–1542. [CrossRef]

75. Xue, J.; Peldszus, S.; Dyke, M.I.V.; Huck, P.M. Removal of polystyrene microplastic spheres by alum-based coagulation-flocculation-sedimentation (CFS) treatment of surface waters. *Chem. Eng. J.* **2021**, *422*, 130023. [CrossRef]

76. Siddique, M.; Soomro, S.A.; Aziz, S.; Jatoi, A.S.; Mengal, A.; Mahar, H. Removal of turbidty from turbid water by bio-cogulant prepared from walnut shell. *J. Appl. Emerg. Sci.* **2016**, *6*, 66–68.

77. Arulmathi, P.; Jeyaprabha, C.; Sivasankar, P.; Rajkumar, V. Treatment of textile wastewater by coagulation–flocculation process using gossypium herbaceum and polyaniline coagulants. *Clean Soil Air Water* **2019**, *47*, 1800464. [CrossRef]

78. Gaikwad, V.; Munavalli, G. Turbidity removal by conventional and ballasted coagulation with natural coagulants. *Appl. Water Sci.* **2019**, *9*, 130. [CrossRef]

79. Momeni, M.M.; Kahforoushan, D.; Abbasi, F.; Ghanbarian, S. Using chitosan/CHPATC as coagulant to remove color and turbidity of industrial wastewater: Optimization through RSM design. *J. Environ. Manag.* **2018**, *211*, 347–355. [CrossRef] [PubMed]

80. Asharuddin, S.M.; Othman, N.; Zin, N.S.M.; Tajarudin, H.A.; Din, M.F.M.; Kumar, V. Performance assessment of cassava peel starch and alum as dual coagulant for turbidity removal in dam water. *Int. J. Integr. Eng.* **2018**, *10*, 185–192. [CrossRef]

81. Zahrim, A.Y.; Dexter, Z.D.; Joseph, C.G.; Hilal, N. Effective coagulation-flocculation treatment of highly polluted palm oil mill biogas plant wastewater using dual coagulants: Decolourisation, kinetics and phytotoxicity studies. *J. Water Process Eng.* **2017**, *16*, 258–269. [CrossRef]