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Recovery of $FeCl_3$ coagulant by acid digestion and Nafion 117 membrane method and its environmental and biological evaluation

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ABSTRACT
Coagulant materials are usually expensive and the purchase, transportation, and maintenance costs are high for all water treatment plants. The disposal of sludge resulting from used coagulants also requires knowledge-based management, and it is necessary to foresee scientific and economic points of view for the disposal of sludge resulting from coagulants in the environment. The present study aimed to design cost-effective and simple Ferrum-based coagulants. So, Fe^{3+} was recovered through acid digestion and the Nafion 117 membrane, then these methods efficiency was compared together. The present study showed that the average recovery rates (%) of Fe^{3+} by acid digestion and Nafion 117 membrane were 73% and 71.5% after 30 and 25 min, respectively. Also, the ratio of return sludge to sulfuric acid was 40:60 during the acid digestion method. According to the results, the Nafion 117 membrane in addition to a significant effect in reducing the concentration of $FeCl_3$ in wastewater did not release sulfuric acid, meaning that reducing the disposal of chemical sludge by Nafion 117 has not environmental negative effects, and can prevent the biological and physical degradation of farms.

Keywords: Water pollutants, Coagulant recovery, Ferric chloride, Wastewater.
Article type: Research Article.

INTRODUCTION
The conventional operation of drinking water treatment includes the processes of coagulation, flocculation, sedimentation, filtration, and disinfection. Coagulation as a physicochemical process is one of the main stages of water purification to destabilize colloidal particles. During the coagulation process, colloidal particles that cause water turbidity are trapped in large masses and are mainly removed in the sedimentation phase or, to a lesser extent, in the filtration phase. The coagulation-flocculation process leads to the production of a large amount of water treatment sludge (WTS; Ahmad *et al.* 2016; Tavakoli *et al.* 2022). Sewage sludge is a mud-like residue resulting from wastewater treatment. These heterogeneous materials can contain various compounds including organic compounds such as nitrogen and phosphorus, micro-organisms, mineral matter, moisture, heavy metals, and pathogens such as viruses and bacteria (Ramzanipour *et al.* 2023). Some components of sewage sludge, including non-toxic organic compounds are recyclable and can be very useful as a fertilizer or soil improver. However, heavy metals with potential toxicity are also present in them, which can accumulate in the environment. The water treatment sludge produced in a water treatment plant (WTP) usually contains organic compounds, minerals (such as fine sand, silt, and clay), and heavy metals (Ahmad *et al.* 2016). Heavy metals, such as chromium, arsenic, and barium can lead to pollution and biological damage if released into the environment (Qu *et al.* 2019). Sewage sludge with high organic carbon content and macro and fine elements (mainly nitrogen and phosphorus) provide a suitable possibility to use as an agricultural fertilizer. However, the high percentage of environmental pollutants such as heavy metals in sludge significantly limits their application (Chung *et al.* 2012).

Aluminum sulfate (alum.), ferric chloride ($FeCl_3$), and poly aluminum chloride (PAC) are usually used as common coagulants to remove heavy metals from the sludge in industry (Mahdavian *et al.* 2018). The recovered sludge by these coagulants is usually used in agriculture. Also, part of it is incinerated and the rest is disposed in the landfill, (Evuti & Lawal 2011). According to the EU Report (Kelessidis & Stasinakis 2012), more than 10 million tons of dry solids (DS) of sewage sludge was produced in 26 EU Member States in 2008, of which approximately 36%, (3.7 million tons DS) was recycled in agriculture. However, the amount of employment of this sludge is different in different countries. For example, according to annual reports, the average employments of recovered sludge in France, Finland, and Swaziland were about 50, <5, and 0%, respectively (Directive 1999; Milieu 2008). The water treatment process requires high amounts of coagulant, which increases the volume of sludge and can limit its usage (Keeley *et al.* 2014). Recovery of coagulant materials from water treatment plant sludge for reuse is one of the important options to reduce the employment of chemicals in the water treatment industry (Keeley *et al.* 2012). The recovery methods of coagulant materials from water treatment plant sludge include acid digestion, alkaline digestion, ion exchange, and membrane separation. However, the combination method is usually used to increase recovery efficiency and achieve results in industries (Qu *et al.* 2019).

Acidic digestion is a method with high efficiency and low cost. However, the resulting process is non-selective and can recover other substances soluble in acidic conditions along with coagulants (Keeley *et al.* 2012; Mahdavian & Ostovar 2018). Alkaline digestion has the same limitations as acid digestion, since there is a large amount of natural organic matter in the recycled solution (Ahmad *et al.* 2016). The ion exchange method as a combination method uses ions to improve the recovery of coagulants after alkaline and acidic digestion (Hamzah *et al.* 2022). The Donnan membrane process (DMP) is a potential gradient process. This process is caused by concentration and the driving force (Parkash & Sengupta 2003). It is not sensitive to fouling by small particles or large organic molecules. A series of tests confirmed that over 70% of Fe^{3+} can be recovered through DMP, and the recovered Fe^{3+} is essentially free of particulate matter, natural organic matter (NOM), and other trace metals. After repeated use in the presence of high concentrations of NOM and suspended solids, there is no significant decrease in Fe^{3+} flux through the membrane and 75% recovery of Fe^{3+} is achieved after 24 hours. In addition, this process is equally effective for concentrating trivalent cations (Asante Sackey *et al.* 2021). DMP is a potential gradient process. This process is caused by concentration and the driving force (Parkash & Sengupta 2003). However, despite the high ability in equilibrium and separation of heavy metal and the selective performance, it usually does not apply to industries (Ben Hamouda *et al.* 2017), since it is a slow kinetic process for ion transport and needs more time than other methods (such as alkaline and acidic digestion) to achieve equilibrium and separation of metal species (Turki & Ben Amor 2017). Integrating DMP with other separation processes can be a practical solution to improve its performance (Asante Sackey *et al.* 2021). DMP selectively recover Fe^{3+} while rejecting organic matter, puts it a step ahead of other metal recovery techniques (Asante Sackey *et al.* 2018). The Nafion 117 cation exchange membrane can be used for the Donnan membrane.

The Box Behnken test matrix determines the interaction effects of input variables for optimal coagulant recovery. The experimental results showed the generated quadratic statistical module was significant with a low p value (< 0.001). Statistical prediction of experimental results shows that recoveries above 85-96% are achievable (Keeley *et al.* 2012). The Nafion membrane was introduced by DuPont from a group of perfluoro sulfonic acid polymers as the most common member of the proton exchange membrane family in the 1960s. Nafion has high proton conductivity. Its structure consists of hydrophobic and hydrophilic regions; this structure is the main factor of Nafion's phase separation (Mehdipour Ataei & Mohammadi 2021). The numerical naming method based on the equivalent weight (EW) is suggested for coding all models of Nafion commercial membranes. Hence, the commercial Nafion membranes include Nafion 112 with a thickness of 50 µm, Nafion 1135 with 88 µm, Nafion 115 with 125 µm and Nafion 117 with 175 µm. The thickness of Nafion membranes affects their performance (Jiang *et al.* 2016). Researches on Donnan membrane processes (DMPs) are expanding and their full potential is not yet understood. The present study aimed to design a cost-effective and simple coagulant based on integrating Nafion 117 as a DPM with Ferric chloride ($FeCl_3$) as a common coagulant.

MATERIALS AND METHODS

The experiments of this research were conducted in the laboratory of Guilan University and the laboratory method was based on the 23rd edition of the 2017 Standard Method. This inquiry included two phases.

Preparation

The water treatment sludge (WTS) was taken from the local water treatment plant in Rasht, Guilan, Iran. The wet sludge was prepared and dried according to the descriptive method by Hamzah *et al.* (2022). After dewatering, the sludge was crushed using a mortar. The sludge was then sieved using a 16 µm- sieve pan. The powdered sludge sample was weighed at a constant weight of 50 g and mixed with 250 mL distilled water. The distilled water was as a solvent.

Acidification of clarifier returns sludge

The coagulant performance was tested through a jar test experiment (Hamzah *et al.* 2022). To obtain correct and optimal results from the economic point of view, in this study, a certain amount of return sludge was added to different volumes of sulfuric acid (98-95% Merck, Darmstadt, Germany) to recover Fe^{+3}. The constant volume of returned sludge and different volumes of sulfuric acid make it easier to reach the desired results. For this purpose, the return sludge volumes of 25 and 100 mL were selected (Mahdavian & Ostovar 2018). Also, sulfuric acid volumes of 2, 4, 6, 10, 15, 30, 35, 50, 55, 65, 75, and 80 mL were prepared to be added to the sludge for 20, 30, 40, 60, and 80 min with 3 replications. These concentrations and times were selected according to Turki & Ben Amor (2017) and laboratory facilities.

Using Nafion 117 membrane

In this phase of the pilot research, two similar chambers were built and a Nafion 117 membrane (Sigma-Aldrich, St. Louis, Missouri, USA) with dimensions of 10 × 10 cm^2 was used between them. The volume of each compartment was 1 L (Asante Sackey *et al.* 2021). In the first chamber, the sludge on which the acid digestion process had been carried out and had an optimal separation percentage at the optimal time, was poured. an aliquot of 1 liter of 1 molar of sulfuric acid was poured into the other chamber. To investigate the performance of the Nafion 117 membrane in transferring Fe^{3+} from the return sludge chamber to the diluted sulfuric acid chamber at 0, 1, 2, 4, 6, and 24 h, sampling was performed in a volume of 100 mL (2 samples, 50 mL each). Sampling was performed at different hours to obtain optimal recovery of Fe^{3+} (Keeley *et al.* 2012; Mehdipour Ataei & Mohammadi 2021).

Data analyze

All analyses were performed using SPSS software (SPSS Statistics V20, IBM Co., New York, US) on the Windows platform (Win. 7 Ultimate × 64, Microsoft Inc., New Mexico, US). The correlation between measured indices and the test variables and also together was evaluated through a probit test with a 95% confidence. In addition, significant differences between averages of measured indices of groups were determined through the one-way analysis of variance (ANOVA) with a 95% confidence (Asante Sackey *et al.* 2018).

RESULTS AND DISCUSSION

The research results of the recovery of $FeCl_3$ coagulant by acid digestion and the Nafion 117 membrane method exhibited that there was a significant correlation between sulfuric acid concentrations and the recovery percentage of Fe^{3+} ($p < 0.01$). The highest recovery rate (%) of Fe^{3+} was related to 80 mL- sulfuric acids. In addition, the ratio of return sludge was significantly increased by the elevated volume of sulfuric acid. The highest ratio of return sludge to sulfuric acid was 24% - 76% in the final mixture. These results are shown in Table 1.

The analysis of data showed there was a significant correlation ($p<0.01$) between reducing the recovery percentage of Fe^{3+} and increasing the volume of sludge; increasing the volume of sludge led to reducing the recovery percentage of Fe^{3+} (Fig. 1). The optimum point of the percentage recovery of Fe^{3+} was at the volume of 25 mL of returned sludge, and the volume of 35 mL of sulfuric acid. The ratio of return sludge to sulfuric acid, the recovery percentage of Fe^{3+}, and time duration were 60/40, 73%, and 40 min respectively. The result showed that the Nafion 117 membrane led to a significant reduction in the concentration of Fe^{3+} in returned sludge (Table 2). The highest recovered rate of Fe^{3+} was 71.5% at 24 h after beginning the test. In addition, the recovery rate of Fe^{3+} at 2, 4, and 6 h after beginning the test were 35.7%, 44.3%, and 52.9%, respectively (Table 2). The highest recovery percentage of Fe Nafion 117 membrane was related to the first 6 h (Fig. 2). The least slope of recovery percentage graph significantly reduced between 6 to 24 h.

Table 1. Effect of sulfuric acid (H_2SO_4) on the recovery rate (%) of Fe^{3+} and ratio of return sludge (Sludge/H_2SO_4).

return sludge (mL)	H_2SO_4 (mL)	Sludge/H_2SO_4	Recovered Fe (%)
25	80	24/76	88
25	75	25/75	87
25	65	28/72	86
25	55	31/70	85
25	50	33/67	75
25	35	40/60	73
25	30	45/55	52
25	15	62/38	49
25	10	71/29	39
25	6	70/30	36
25	4	80/20	32
25	2	92/8	28
25	0	100/0	0

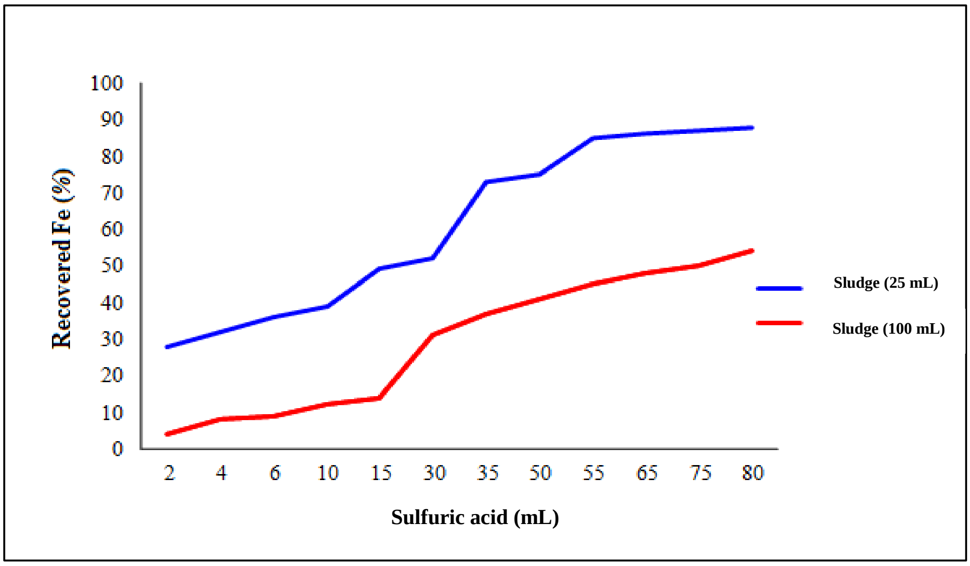

Fig. 1. The correlation between volume of sludge and the recovery percentage of Fe^{3+}.

Table 2. The percentage recovered of Fe^{3+} (R. P. Fe^{3+}) through the Nafion 117 membrane.

Time (*h*)	Average concentration of Fe (mg)		R. P. Fe (%)*
	sludge digested	After Nafion 117 membrane	
0	505.5	0	0
2	361.2	180.4	35.7
4	318.1	223.8	44.3
6	276.3	267.6	52.9
24	261.3	361.4	71.5

Note: The numbers of samples were 12th

The recovery of coagulant and coagulant aid can be a particular way to reduce volume of sludge and supplying coagulant and coagulant aid in water treatment plants (Keeley *et al.* 2012, Wei *et al.* 2000). The release of high volumes of chemical waste in the environment by treatment plants can threaten ecosystems, especially aquatic environments, since aquatic environments are the last destination of chemical pollutants. Results of the present study showed 71.5% of Fe^{3+} ($FeCl_3$) recovered by Nafion 117 membranes after 24 h. Parkash & Sengupta (2003) reported that Donnan membrane process (DMP) was effective in recovering Fe^{3+} based coagulants (about 70%). Also, they stated that after repeated usage of DMP in the presence of a high concentration of natural organic matter (NOM) and suspended solids, there was not a noticeable decline in ion flux through the membrane, and the membrane surface practically was no fouling. However, Guney *et al.* (2008) reported that the increased suspended solids and organic matter contents in sludge can hurt metal ion removal efficiency over time. The result of the present study showed that the slope of the Fe^{3+} recovery percentage graph was significantly reduced between 0 to 24 h. This decrease in slope can be caused by the accumulation of suspended solids and organic matter contents on Nafion 117 membranes surface.

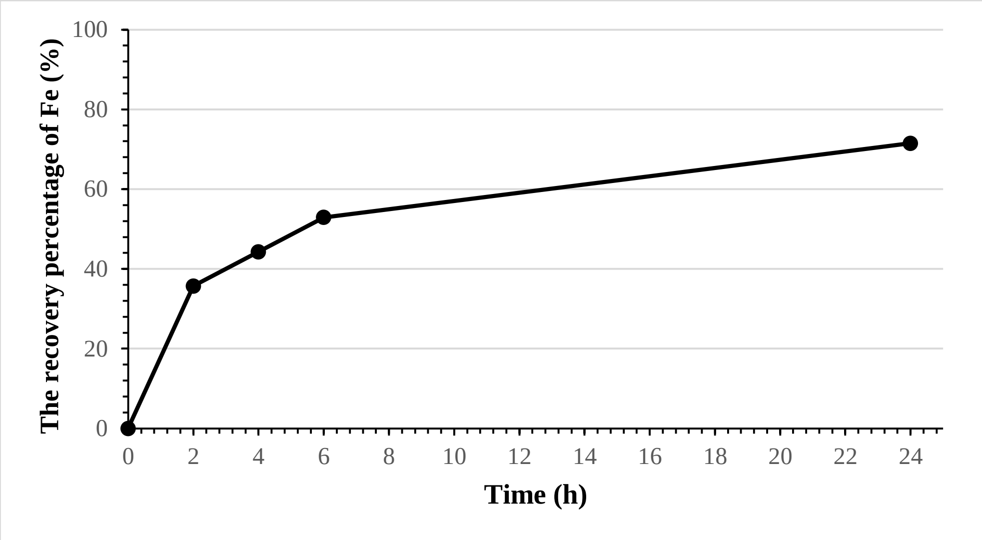

Fig. 2. The trend of changes of recovery percentage of Fe^{3+} through Nafion 117 membrane during 24 h.

Acidic digestion is a non-selective method for the recovery of heavy metals, such as iron, aluminum, and silver. In addition, processing large volumes of acidic leachate can be expensive (Oliver & Carey 1976). Sulfuric acid has high toxicity for most known organisms (Trent *et al.* 1978). It can reduce pH and decrease the ability of aquatic organisms to effectively absorb dissolved oxygen (Araoye 2009). In addition, acidic leachate has high volume of ferrous sulfate heptahydrate ($FeSO_4^{*}7H_2O$) and Fe^{3+} (Dann 2009). Dalzell & Macfarlane (1999) reported ferrous sulfate 96 hours after exposure, in addition to increasing the mortality rate of brown trout (*Salmo trutta*), leading to oxidative stress and physical clogging of gills and damage. Also, Da Costa *et al.* (2019) reported that Fe^{+2} and Fe^{3+} significantly reduced survival rate of a tropical fish (*Leporinus friderici*) during the LC_{50} - 96 h test. In addition, the results of the present study exhibited that there was a significant correlation between the elevated volume of sludge and the reduced recovery rate (%) of Fe^{3+}. Finally, the upraised recovery rate of Fe^{3+} required an elevation in the concentration of sulfuric acid. The optimum recovery point of Fe^{3+} can significantly reduce the cost of the coagulant recovery process (Nayeri & Mousavi 2022). In addition to economic efficiency, the optimum recovery point of Fe^{3+} can reduce the volume of sludge, volume of coagulants, and heavy metal residue (Keeley *et al.* 2014). The optimal point is highly dependent on the exposure time, the physical conditions of the sludge, such as temperature, pH, and volume (Evuti & Lawal 2011). Therefore, different ratios have been proposed for the optimum point of the percentage recovery of Fe^{3+}. The results of the present study revealed that the optimum condition to economic recovery of Fe^{3+} was the 25 mL of returned sludge, 35 mL of sulfuric acid, the ratio of 60/40 (gram of return sludge to mL of sulfuric acid), and the of Fe recovery rate of 73% in 40 min.

CONCLUSION

The present work revealed that the study of Nafion 117 membranes as a Donnan membrane process (DMP) exhibited a significant effect on the recovery of Fe^{3+}. Nafion 117 membranes can recover 71.5% of Fe^{3+} from returned sludge after 24 h. In addition, in comparison with the acid digestion method, Nafion 117 membranes did not display acidic leachate and toxic residue. However, this method required more time than the acid digestion method. The results of the present study can be used as the base of future studies and use in wastewater management in water treatment plants. Finally, the evaluation effect of environmental changes, such as pH and temperature on the efficiency of this method can be the title of future studies.

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Data availability: The datasets in this study are available from the corresponding author on reasonable request. All data and materials are available for publication.

Declarations
Ethics approval. Institutional guidelines for the ethical issue were followed. The experimental protocol was authorized by the Institutional Animal Care and Ethics Committee of Islamic Azad University, Lahijan, Iran
Consent to participate. Not applicable.
Consent to publish. All authors give consent for publication.
Conflicts of interest. The authors declare no conflict of interest.
Code availability. Not applicable.

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