PERFORMANCE EVALUATION OF SINGLE AND COMBINED EFFECTS OF CHEMICAL ADSORBENTS FOR OPTIMUM REMOVAL OF HEAVY METALS FROM GROUNDWATER

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ABSTRACT

The groundwater has become more susceptible to heavy metal pollution due to human activities like landfill leachate, the use of chemical fertilizer in agriculture, underground pipeline leakage, underground chemical, and petroleum products storage, etc. Rajshahi, one of the major cities in Bangladesh, has been facing the problem of groundwater contamination by heavy metals in recent years, especially, Manganese (Mn) contamination is more severe in the groundwater of RCC than any other heavy metals. In this study, three chemical adsorbents (Ferric Chloride ($FeCl_3$), Ferric Sulfate ($Fe_2(SO_4)_3$), and Aluminium Sulfate ($Al_2(SO_4)_3$)) were selected for removing the Mn from groundwater. The experimental investigation was conducted in three phases. In the first phase, three selected adsorbents were evaluated individually to determine their optimum dose for the removal of Mn in 24 hrs. In the second phase, the selected optimum doses for each adsorbent were used to evaluate the removal percentage of Mn with the selected contact times (5 minutes, 10 minutes, 15 minutes, 20 minutes, 30 minutes, 1 hour, 2 hours, and 4 hours). In the third phase, the adsorbents are combined together with their identified optimum doses, and the removal percentage with respect to contact time is determined. The result showed that the combined effect of the adsorbents is more effective than their individual effect in removing Mn from groundwater. Moreover, the optimum doses for $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$ and $FeCl_3$ were found to be 250 mg/L, 150 mg/L and 100 mg/L with manganese removal percentage of 100%, 95.42% and 86.72% respectively. For the combined phase of the chemical adsorbents, the optimum dose was found to be 75 mg/L with 100% removal of Mn from groundwater. Additionally, the pollutant removal trend for both individual and combined effects of adsorbents followed a logarithmic curve.

Keywords: *Chemical absorbents, Groundwater treatment, Heavy metal, Pollutant removal percentage, Rajshahi City*

1. INTRODUCTION

Groundwater is the world's biggest natural reservoir, providing water for drinking, agriculture, and industry. Bangladesh extracts about 32 km^3 of groundwater each year, 90% of which is used for agriculture and 10% for household and industrial uses together, accounting for 4% of worldwide groundwater extraction (Shamsudduha et al., 2020). In Rajshahi City and its suburbs, groundwater contamination has been identified as a serious issue. The key issue is the high iron concentration, which is in the range of 0.4-3.5 mg/L in the RCC region and 0.23-7.12 mg/L outside the RCC area, above the national drinking water requirements of 0.3-1.0 mg/L in both cases (Helal Uddin et al., 2011). Manganese concentrations were also elevated, varying from 0.1-1.52 mg/L in the RCC region to 0.23-2.40 mg/L outside the area, above the 0.1 mg/L drinking water limit (Helal Uddin et al., 2011). Total dissolved solids and arsenic levels across most specimens were higher than the recommended level for potable water in Rajshahi City (Rasul & Jahan, 2010).

Several technologies are adopted for the treatment of water such as coagulation and flocculation, adsorption, chemical precipitation, ion exchange, membrane filtration, sand filtration, activated carbon adsorption, and up-flow anaerobic packed bed reactors (UAPB) (Shahi et al., 2020); (Loloei et al., 2014). The UAPB often causes sulfide toxicity to the plants. (Shahi et al., 2020). In media filtration chemical precipitation processes are not suitable when the metal ion concentration is relatively low and can generate large amounts of sludge (Tang et al., 2016) The ion exchange method is really expensive, particularly when treating a large amount of wastewater at a large scale possessing heavy metals in lower concentrations (Fu & Wang, 2011). Membrane filtration technology has the complexity of membrane fouling as well as low permeate flux. The initial capital investment is really high in the case of electrochemical technologies (Fu & Wang, 2011).

The chemical coagulation process has been given priority for many conveniences for heavy metal removal and has been used intensively for the last decades. (Loloei et al., 2014)conducted a comparative study of alum and ferric sulfate for the treatment of industrial wastewater. They showed that when Polyacrylamide and Poly Ferric Sulfate are applied with Alum, the removal percentage of COD is increased from 68% to 82%. Ferric sulfate had the capability to reduce 62% COD and turbidity up to 95%. (Abu Bakar & Halim, 2013) showed that the poly aluminum chloride coagulant successfully removed 83%, 98%, and 63% of Zn, Fe, and Ni respectively from wastewater. In another study, turbidity, COD, color, and TSS removal percentages were achieved at 94.0%, 43.1%, 90.7%, and 92.2% respectively for leachate treatment using poly aluminum chloride (PAC) and alum coagulants (Ghafari et al., 2009).

Several studies were conducted for the removal of turbidity, BOD, COD, color, TSS, nitrogen, and phosphorus from water/wastewater. However, very limited study was undertaken for the removal of heavy metals (e.g. Cr, Cd, Pb, As, Fe, Cu, Mn, etc.) using coagulation from groundwater. Hence, the development of a treatment strategy by indicating effective coagulation types and corresponding optimum process parameters value required for heavy metal treatment is critically important to protect public health.

2. METHODOLOGY

2.1 Study Sites

Rajshahi is one of the major metropolitan cities in Bangladesh. Rajshahi City Corporation (RCC) is one of the major self-governing cities in Bangladesh. Geographically, the latitude and longitude of Rajshahi City lie between 24°20' N to 24°24' N and 88°32' E to 88°40' E. It is situated within the Barind tract, 23m above sea level. The approximate area under Rajshahi City Corporation is 48 km^2. According to the Bangladesh Population Census 2001 (Bangladesh. Parisaṃkhyāna Byuro. Statistics and Informatics Division, 2013.), the population of Rajshahi city was 3,88,811. But the population had increased to approximately 4,49,756 according to the Bangladesh Bureau of Statistics, 2011

(BBS, 2011). The city is located on the bank of the Padma River. There are 30 wards in the Rajshahi City Corporation.

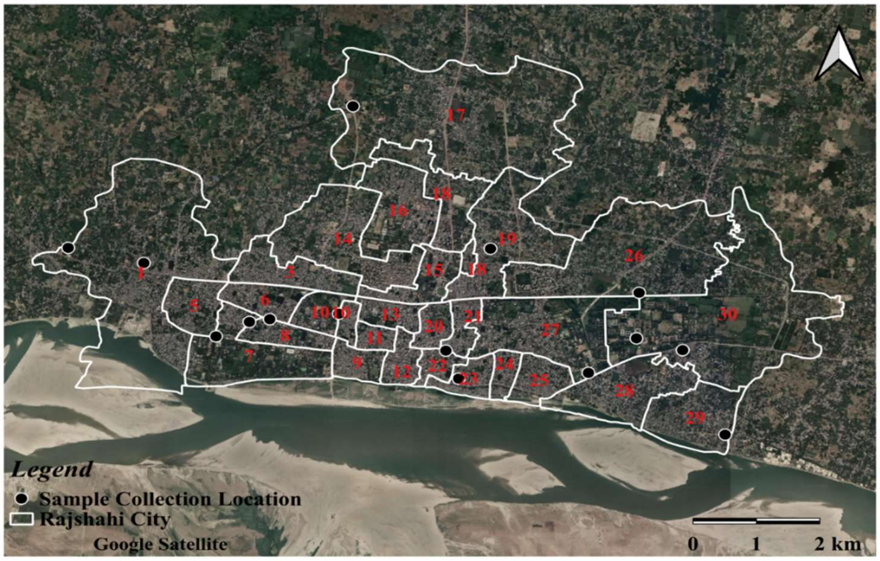

Figure 1: Rajshahi City Corporation

2.2 Sample collection

The sample was collected from the tubewell of 17 different wards of RCC whose depth was approximately 100-120 ft. The tube wells have been continuously used by the locals for drinking and other purposes since its formation. Water was drawn from each tube well for 3–4 minutes before taking the samples. The samples were then placed in previously cleaned and dried plastic bottles for storage. The water samples were then carefully transported to the lab immediately.

Figure 2: Sample Collection

2.3 Selection of water quality parameters

The sample that was collected from Sagorpara, ward no 22, was tested to determine if it contained any heavy metals: Iron (Fe), Copper (Cu), Lead (Pb), Manganese (Mn), Arsenic (As), and Cadmium (Cd). The test was undertaken using an AAS (Atomic Absorption Spectroscopy) machine in the

Environmental Engineering Laboratory of Rajshahi University of Engineering and Technology. This location was chosen for sample collection due to it being closest to the laboratory.

Figure 3. AAS (Atomic Absorption Spectroscopy) machine

2.4 Selection of chemical adsorbents

The chemical adsorbents were purchased in plastic-sealed bottles through the university procurement process funded by the University Grants Commission (UGC) (Figure 5). The adsorbents were kept in a cool and dry place to avoid contamination.

Figure 5(a). Aluminium Sulphate

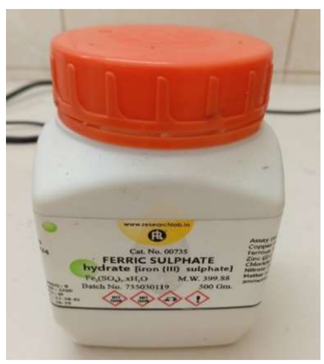

Figure 5(b). Ferric Sulphate

Figure 5(c). Ferric Chloride

2.5 Experimental Phase

The removal rate of Mn due to chemicals is evaluated. Three chemical adsorbents are added individually and the removal rate of Mn is determined at 24 hours. The dose where there is a maximum removal rate of Mn is taken as their optimum dose. After that, the removal rate at predetermined time intervals is evaluated for optimum doses of adsorbents.

The optimum doses of adsorbents are mixed at their individual optimum dose ratio to evaluate the combined optimum dose. The combined natural adsorbents are mixed at different doses in groundwater and the optimum dose for the combined effect of chemical adsorbents is determined. After that, the removal rate at predetermined time intervals is evaluated for optimum doses of adsorbents.

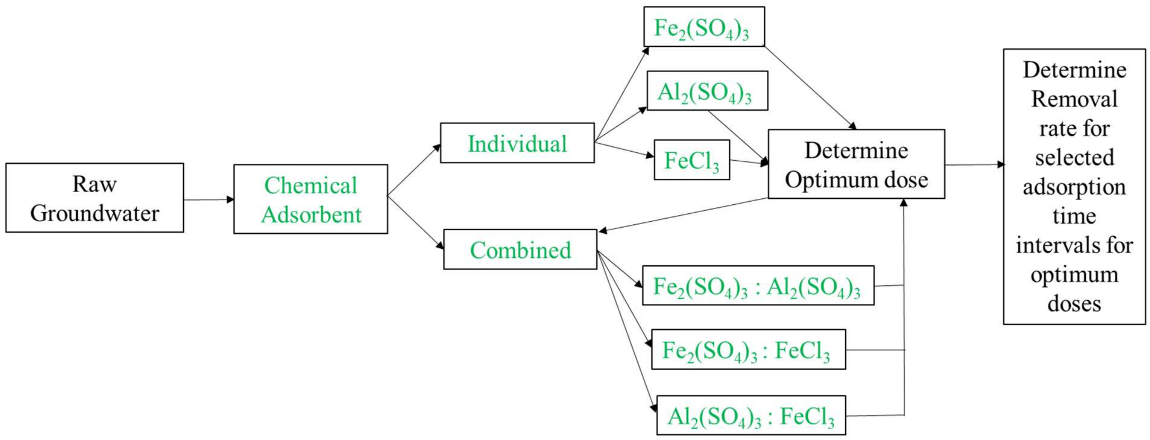

Figure 6: Experimental Phases

2.6 Experimental Set-up

There are a total of 4 steps in this study. First, the adsorbents are added to the fresh groundwater sample. Then, the samples were placed in a mechanical shaker for 30 minutes at 300-350 rpm. After 30 minutes, the samples are placed in a resting place for a specific time. After the desired time, the samples were filtered using a filter machine and Whatman filter paper of side 11 μm.

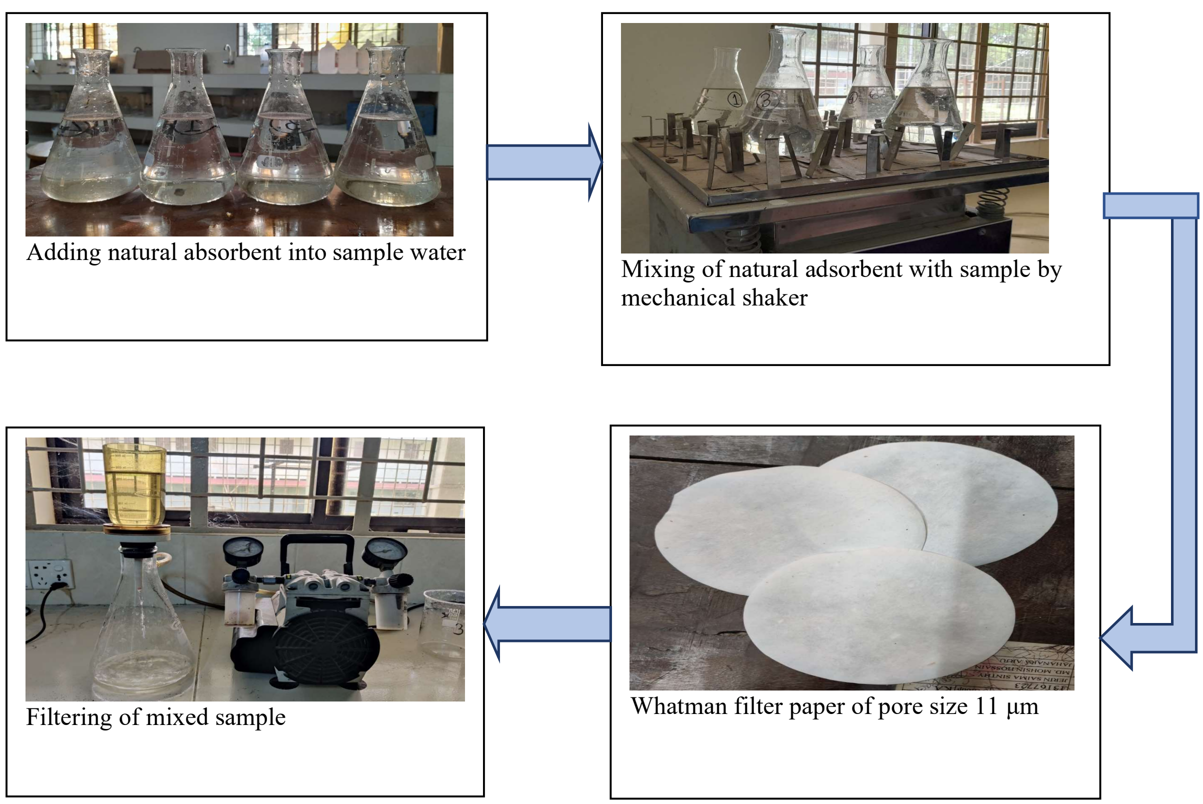

Figure 7: Experimental Set-up

3. RESULTS AND DISCUSSIONS

3.1 Water quality parameters

The groundwater from the tube well was found to be extremely contaminated by manganese (Mn). The groundwater of most of the wards has crossed the Bangladesh standard limit of Mn in drinking water which is 0.1mg/L. Again, the content of Fe in groundwater was also found to be higher than the permissible limit of Fe in drinking water, which is 0.3–1 mg/l based on Bangladeshi guidelines. The other heavy metals in the raw sample were found to be zero or way below their allowable limit in drinking water.

All the selected adsorbents alone and their combined doses were found very effective for removing 100% of Fe from the groundwater in 5 minutes. The removal of Mn varied for different adsorbents and their combined effect. Therefore, the variation in the removal of Mn due to the effect of natural adsorbents is mainly discussed here.

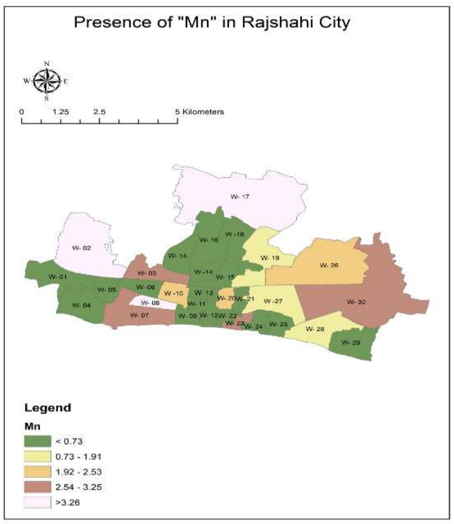

Figure 8: Distribution of Mn in Rajshahi City

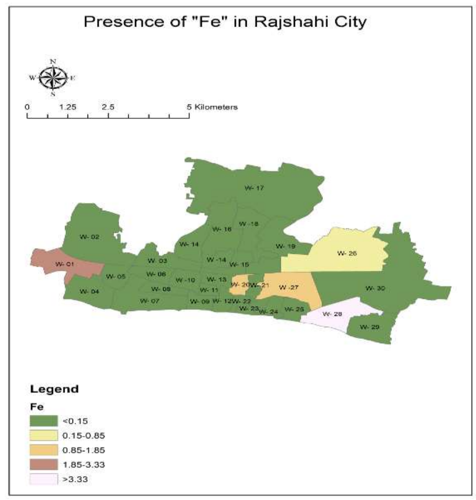

Figure 9: Distribution of Fe in Rajshahi City

3.2 Determination of the optimum doses for individual chemical adsorbents

Figure 10 shows the effect of different chemical adsorbents in different doses on the removal percentage of manganese from groundwater. Different adsorbents showed different optimum doses, where maximum removal percentage was observed.

For $Fe_2(SO_4)_3$, the removal percentage increases with the increasing doses. $Fe_2(SO_4)_3$ removes 100% Mn from groundwater at the dose of 250mg/L.

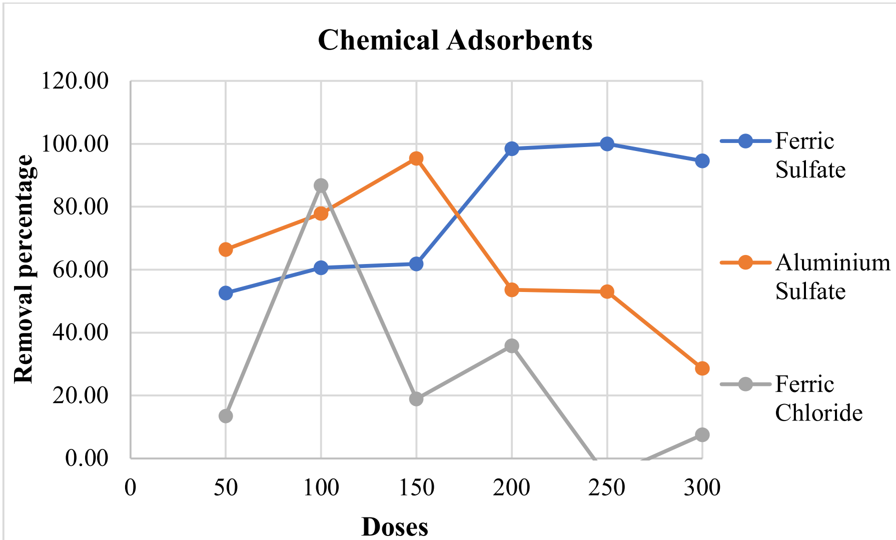

Figure 10: Removal percentage of Mn with different doses due to chemical adsorbent

For $Al_2(SO_4)_3$, the removal percentage decreases with increasing doses after reaching an optimum point. The maximum removal percentage was 95.42% at the dose of 150mg/L.

However, for $FeCl_3$, the removal percentage shows an undefined pattern. $FeCl_3$ is highly volatile at moisture. The maximum removal percentage was 86.72% at the dose of 100mg/L.

Table 1: Maximum removal percentage at optimum doses

Absorbent	Maximum removal percentage	Optimum Dose(mg/L)
$Fe_2(SO_4)_3$	100%	250
$Al_2(SO_4)_3$	95.42%	150
$FeCl_3$	86.72%	100

Figure 11 shows the Mn removal trend was evaluated at optimum doses over the period of 24 hours. It was evident that the removal trend of all the combinations of chemical adsorbents follows a logarithmic trend.

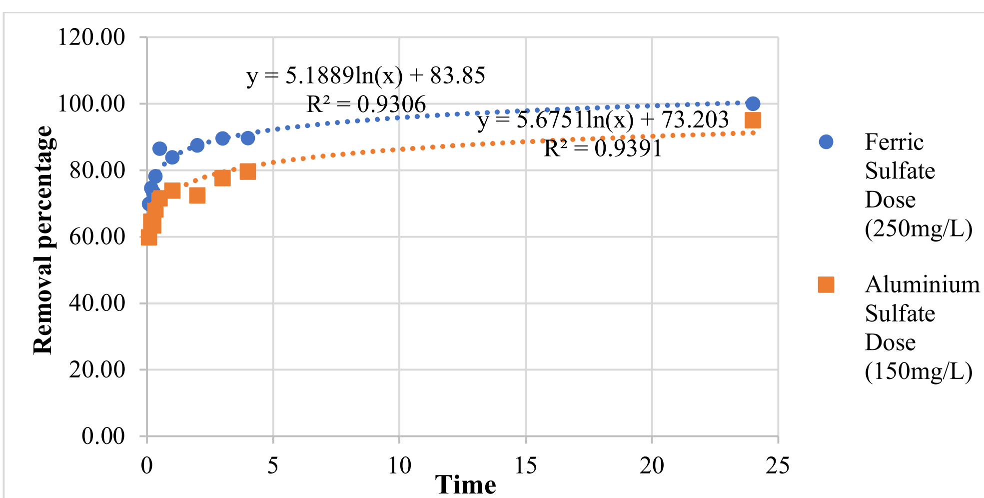

Figure 11: Mn removal trend at optimum doses

3.3 Determination of the optimum doses for combined chemical adsorbents

Due to $FeCl_3$ being highly volatile at moisture, the other two chemical adsorbents are used to evaluate the combined effect of chemical adsorbents.

Figure 12 shows the combined effect of chemical adsorbents in different doses on the removal percentage of manganese from groundwater. The two chemical adsorbents are paired together in one combination with the ratio of their optimum doses.

For $Fe_2(SO_4)_3$: $Al_2(SO_4)_3$, the removal percentage varies with time. The removal percentage of Mn shows an irregular trend. The maximum removal percentage was 100% at the dose of 75mg/L.

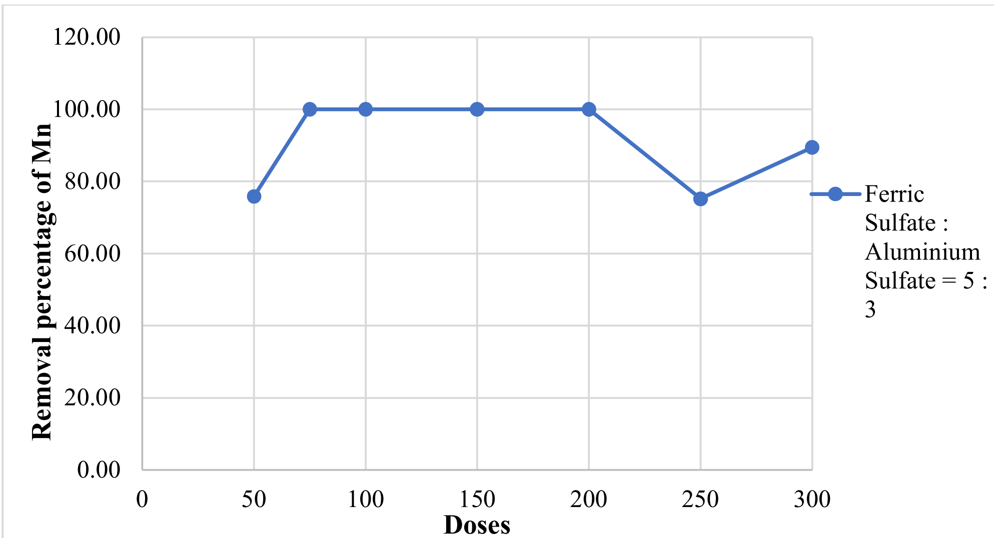

Figure 12: Removal percentage of Mn with different doses due to combined chemical adsorbent

Table 2: Maximum removal percentage at optimum doses

Absorbent	Maximum removal percentage	Optimum Dose(mg/L)
$Fe_2(SO_4)_3$:$Al_2(SO_4)_3$	100%	75

Figure 13 shows the Mn removal trend was evaluated at optimum doses over the period of 24 hours. It was evident that the removal trend for the combination of chemical adsorbents follows a logarithmic trend.

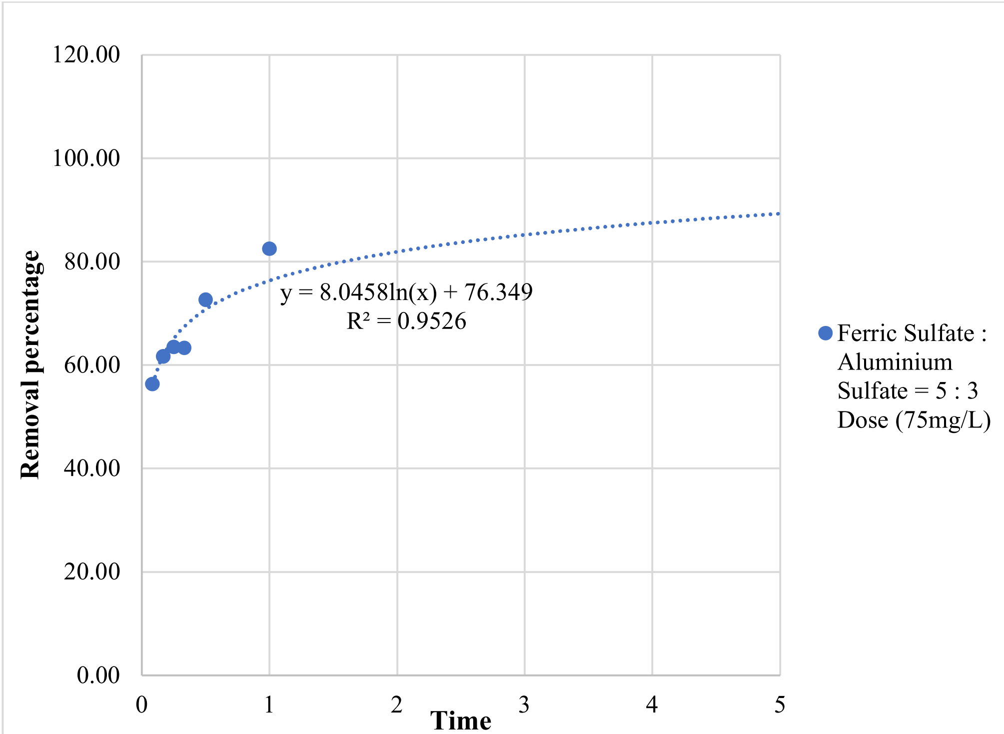

Figure 13: Mn removal trend at optimum doses

4. CONCLUSION AND FUTURE SCOPE

This study shows the groundwater of Rajshahi City is majorly polluted by Mn and Fe among all the heavy metals. In this study, the individual and combined effects of chemical adsorbents are evaluated. The combined effect of the two selected chemical adsorbents works more efficiently than their individual effect in removing Mn from groundwater. At an optimum dosage of 150 mg/L, 250 mg/L, and 100 mg/L, the chemical adsorbents $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $FeCl_3$ removed 95.42%, 100%, and 86.72% of Mn from groundwater, respectively, while the combined effect of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ showed 100% removal of Mn at 75mg/L. Additionally, the Mn removal trend for both individual and combined effects of chemical adsorbents follows a logarithmic trend. The developed empirical model will enable the treatment system designer to choose the effective adsorbents and set their target removal percentages of pollutants.

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REFERENCES

Abu Bakar, A. F., & Halim, A. A. (2013). Treatment of automotive wastewater by coagulation-flocculation using poly-aluminum chloride (PAC), ferric chloride (FeCl3) and aluminum sulfate (alum). *AIP Conference Proceedings*, *1571*, 524–529. https://doi.org/10.1063/1.4858708

Bangladesh. Parisaṃkhyāna Byuro. Statistics and Informatics Division. (n.d.). *Economic census 2013 : district report*.

BBS. (2011). Statistical Yearbook of Bangladesh- 2011, 31st Edition. In *Bangladesh Burea of Statistics*.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. In *Journal of Environmental Management* (Vol. 92, Issue 3, pp. 407–418). https://doi.org/10.1016/j.jenvman.2010.11.011

Ghafari, S., Aziz, H. A., Isa, M. H., & Zinatizadeh, A. A. (2009). Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. *Journal of Hazardous Materials*, *163*(2–3), 650–656. https://doi.org/10.1016/j.jhazmat.2008.07.090

Helal Uddin, S. M., Mostafa, M. G., & Haque, A. B. M. H. (2011). Evaluation of groundwater quality and its suitability for drinking purpose in Rajshahi City, Bangladesh. *Water Science and Technology: Water Supply*, *11*(5), 545–559. https://doi.org/10.2166/ws.2011.079

Loloei, M., Nekonam, G., Alidadi, H., & Kor, Y. (2014). Study of the coagulation process in wastewater treatment of dairy industries. *International Journal of Environmental Health Engineering*, *3*(1), 12. https://doi.org/10.4103/2277-9183.132684

Rasul, M. T., & Jahan, M. S. (2010). Quality of Ground and Surface Water of Rajshahi City Area for Sustainable Drinking Water Source. *Journal of Scientific Research*, *2*(3), 577. https://doi.org/10.3329/jsr.v2i3.4093

Shahi, N. K., Maeng, M., Kim, D., & Dockko, S. (2020). Removal behavior of microplastics using alum coagulant and its enhancement using polyamine-coated sand. *Process Safety and Environmental Protection*, *141*, 9–17. https://doi.org/https://doi.org/10.1016/j.psep.2020.05.020

Shamsudduha, M., Joseph, G., Haque, S. S., Khan, M. R., Zahid, A., & Ahmed, K. M. U. (2020). Multi-hazard Groundwater Risks to Water Supply from Shallow Depths: Challenges to Achieving the Sustainable Development Goals in Bangladesh. *Exposure and Health*, *12*(4), 657–670. https://doi.org/10.1007/s12403-019-00325-9

Tang, X., Zheng, H., Teng, H., Sun, Y., Guo, J., Xie, W., Yang, Q., & Chen, W. (2016). Chemical coagulation process for the removal of heavy metals from water: a review. *Desalination and Water Treatment*, *57*(4), 1733–1748. https://doi.org/10.1080/19443994.2014.977959