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RESEARCH ARTICLE

Enhancing the vanadium recovery from heavy fuel fly ash by using Tri Sodium Citrate as a chelating agent in Alkaline Solution

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ABSTRACT

Sodium carbonate exhibits high selectivity for vanadium and low vanadium recovery rate (43%) from the fly ash of Al-Dura thermal power plant (Baghdad, Iraq) under standard conditions (35 ℃ , 12 hrs, 1M Na2CO3, L/S=10). The recovery increases to 57% in the presence of 0.005M KMnO4. This study explores the role of tri-sodium citrate (0.1M) as a chelating agent in enhancing recovery, achieving up to 85% recovery under the same conditions. Vanadium was precipitated as ammonium metavanadate (NH4VO3) by adjusting pH to 5 using NH4Cl and heating to 50 ℃ for 6 hrs. The precipitate was roasted at 650 ℃ for 2 hrs to obtain vanadium pentoxide (76% purity). The controlling step in vanadium recovery is the chemical reaction rate on the surface of fly ash, as determined by the unreacted-core model. The activation energy for the reaction is (8.47kJ/mole) at a temperature range (35-60 ℃).

Keywords: Vanadium recovery, fly ash, tri-sodium citrate , sodium carbonate, unreacted-core model

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1. Introduction

Vanadium is one of the important elements in industry; it is used in many industrial applications such as the production of alloys (ferrous and non-ferrous), catalysts used in chemical industries, energy storage batteries, spacecraft, and metal smelting furnaces [1-3]. Vanadium enhances alloy strength and wear resistance [2,4], and it was one of the elements where presence in the earth crust at low concentration [5], in which vanadium exists in various forms with minerals [6]. The rising demand for vanadium in many industries in recent years has resulted in the depletion of natural vanadium sources, prompting the search for alternative sources. It has been found that fly ash, black shale, stone coal, spent catalysts, and smelting residues contain significant amounts of vanadium [7-10]. Fly ash is a by-product of heavy fuel combustion in power plants and may serve as an alternative vanadium source [11]. The quantities of fly ash increase annually due to the continuous demand for electrical energy [12], on the other hand it requires a huge area via its low density [13], in addition to its low density, fly ash characterized by containing many toxic metals which leach into soil, potentially groundwater and entering the food chain , which means there is a negative environmental and health impact [14]. For the economic and environmental consideration, vanadium is recovered or removed from fly ash. The recovery process is carried out using acid, alkaline, water, chelating agents and microorganisms [15-21]. The recovery rate of vanadium from fly ash using alkaline solution is lower than acidic media, but it has good selectivity for vanadium from its compounds and is easy to precipitate from its solutions [22]. The current study consists of the use of sodium carbonate as an alkaline material to recover vanadium from fly ash Al-Dura thermal power plant (Baghdad, Iraq). Sodium carbonate exhibits high selectivity for vanadium and low vanadium recovery rate, as an attempt to increase vanadium rate, in which the tri sodium citrate (TSC) will be added as an organic chelating agent to enhance recovery. TSC is readily biodegradable, posing minimal environment risk.

2. Experimental

2.1. Material

The fly ash was obtained from the Al-Dura thermal power plant (Baghdad, Iraq), while the chemicals used are sodium carbonate (99%) from Prolabo , potassium permanganate (97%) from Science, tri sodium citrate TSC (99%) from (NCP), nitric acid (65%) from Fisher, ammonium chloride (99.5%) from sigma Aldrich.

2.2. Procedure

The fly ash is dried of moisture by heating it to a temperature of (120 C°) for 4 hours. The fly ash particles used have a diameter of less than 50 µm and were obtained using standard mesh sieves(50 µm). The fly ash was mixed with a sodium carbonate solution at varying concentrations in the presence or absence of potassium permanganate and tri-sodium citrate in a 1-liter glass flask with continuous mixing at a stirring rate (200 rpm). The effect of the following parameters was investigated: temperature, leaching time, potassium permanganate concentration, TSC concentration, and liquid-to-solid(L/S) ratio. Nitric acid was added to the solution to precipitate aluminum. Ammonium chloride was added to the solution to obtain ammonium metavanadate (AMV), which was roasted in an oven to obtain vanadium pentoxide. Morphological and elemental analyses were conducted using SEM and EDS (Thermo Fisher, Czech Republic) by taking an average measurement of five readings from multiple locations for each sample.

3. Results and discussion

3.1. Characteristics of fly ash

As determined by EDS was shown in **Table 1** and **Figure 1** the predominant elements in the fly ash samples were carbon , oxygen , and sulfur. The element aluminum , silicon iron , copper , and vanadium were identified at low concentration. As seen in **Table 1**, the vanadium content is about 0.5 wt.% , which is an encouraging quantity for the leaching of vanadium from the fly ash. The carbon content in fly ash approximately half because fly ash is produced from the combustion of hydrocarbon material, which are primairly composed of carbon and hydrogen.

Table 1. Main element of fly ash ore

Element	C	O	Al	Si	S	V	Fe	Cu
Weight %	54.6	30.7	0.1	0.1	11.7	0.5	1.3	0.5

The (pH) of the fly ash solution was measured and found to be (10.5) by used (pH) meter (Hanna instruments, India) , indicating that the fly ash solution possesses a basic nature, making its use suitable for soil improvement and adjusting soil acidity. The elements composition for the fly ash as shown in EDX analysis.

Figure 2 A shows SEM image for the fly ash, the morphology of the particles are irregular porous shape, and the image confirms that the particle of fly ash ranged between (10-50)µm, and contains small pores with few micrometers in diameter by using SEM device (Thermo Fisher, Czech Republic). These small pores were formed during combustion process of heavy oil. The porous structure may be because of present of a few irregular fragments, debris of microsphere, and cohesive bodies. The presence of these pores further increases the specific surface area of the fly ash and enhances its adsorption ability [23]. This structure makes fly ash suitable for use as an adsorbent in some industrial applications after removing its harmful elements.

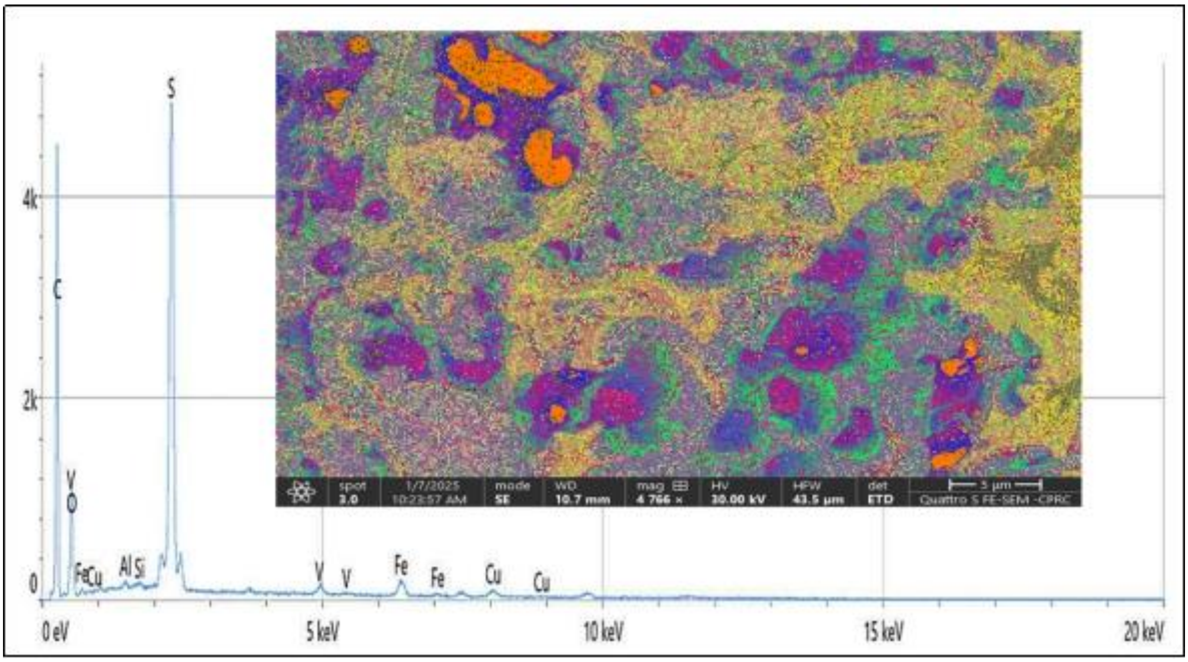

Figure 1. Elemental composition for fly ash as shwon in EDX anlysis, inset figure show the elemrntal mapping for the fly ash

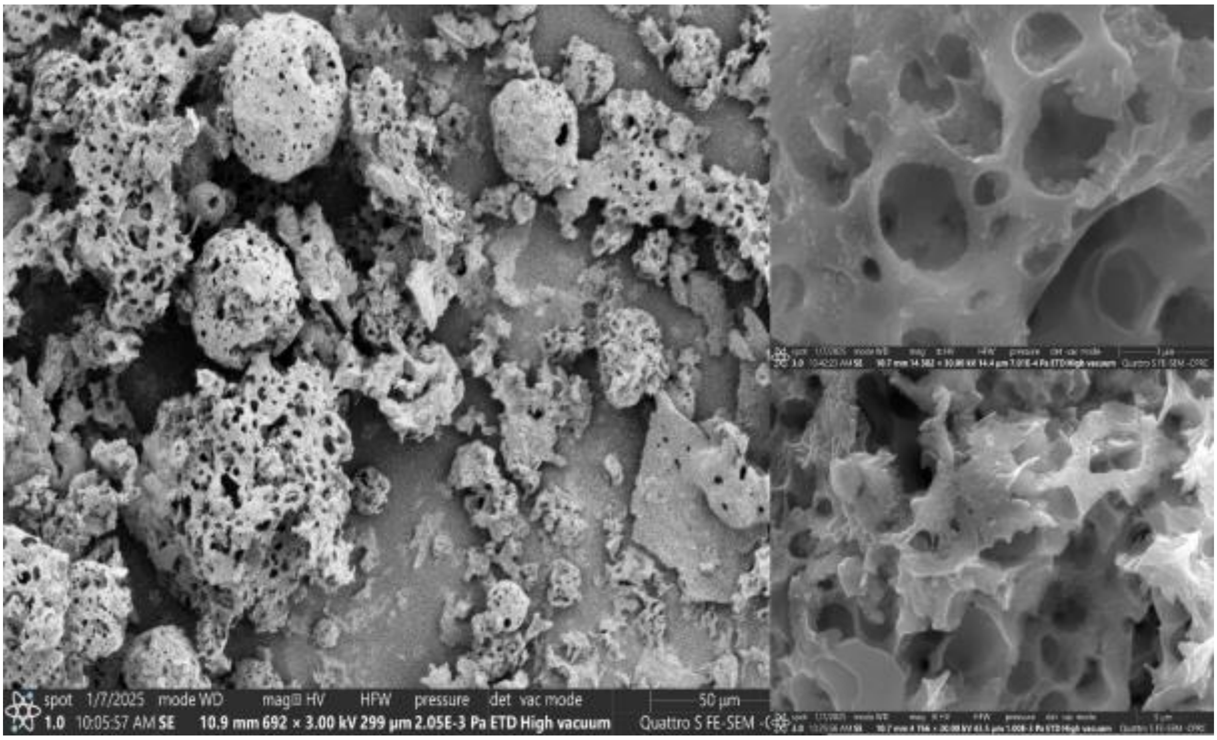

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Figure 2. SEM image of fly ash ore

3.2. Leaching fly ash

To recover vanadium from fly ash, it is preferable to use an alkaline solution rather than acidic solutions, particularly sodium carbonate solution, due to its high selectivity for vanadium over other elements present in the fly ash[12]. However, the recovery rate is lower compared to acidic solutions and some other alkaline solutions (NaOH) [12]. The use of TSC will be added to the sodium carbonate solution here to increase the rate of vanadium recovery from the fly ash. The solutions of (TSC) have a mild alkaline (pH=7.5-9) which enhances the desired alkaline medium for vanadium recovery. When dissolving TSC in water, it will dissociate into three sodium ions (Na^+) and one citrate ion ($C_6\ H_5O_7{}^{-3}$), which possesses three carboxyl groups and one hydroxyl group.

$$C_6H_5Na_3O_7 \rightarrow 3Na^{+1} + C_6H_5O_7^{-3} \tag{1}$$

This property enables it to act as a chelating agent, contributing to the enhancement of vanadium recovery from fly ash [24]. The biodegradation of TSC is easy and depends on the air environment, microbial activity, and temperature of the solution, producing substances that have no negative impact on the environment [24]. To determine the best conditions for recovering vanadium from fly ash using sodium carbonate and TSC, the effects of sodium carbonate concentration, TSC concentration, oxidizing agent, temperature, time, and the ratio of solution to fly ash were studied.

Figure 3 shows the impact of using sodium carbonate on vanadium recovery, as seen the vanadium recovery reached 42% at 1M Na_2CO_3, while it reached 66% when using 0.1M TSC with 1M Na_2CO_3. The increase in the concentration of sodium carbonate in the solution leads to an increase in the concentration of carbonate ions, which results in a higher likelihood of contact with the sites of vanadium presence in fly ash, thereby contributing to an increase in the recovery rate of vanadium. Further increases above 1M result in minimal recovery gain due to saturation of active sites. There is a slight increasing in the recovery rate due to the presence of few vanadium sites that will not be touched by the solution ions. There are many reports that show that when using different types of surfactants in alkaline solutions such NaOH, and Na_2CO_3, the vanadium content in leaching solution increased to 39% in comparison without surfactants [25-26] , so it may be concluded that TSC works here as a surfactant.

It is also observed on **Figure 4**; the recovery percentage of vanadium increases with the increase in the concentration of (TSC) while keeping the concentration of sodium carbonate constant. The recovery percentage changes from (50%) to (66%) when the concentration of (TSC) varies from (0.01M to 0.1M). This is attributed to the increased citrate ions in solution, which acts as a chelating agent that binds with the vanadium present in the fly ash to form a complex compound in the solution, as below equation:

$$3FA(V)+R\text{-}(COONa)_3 \rightarrow 3FA(Na)+R\text{-}(COOV)_3 \tag{2}$$

Figure 5 shows the impact of temperature on vanadium recovery, while keeping the other parameters constant (leaching time 12 hr., L/S =10, 1 M Na_2CO_3, and free $KMnO_4$). The recovery efficiency is increasing with temperature. The recovery percentages at 60 ℃ are 96%, and 70% in case of presence, and absence of 0.1 M TSC respectively. The temperature increasing leads to an increase in the vibrations of carbonate and citrate ions in the solution, and thus the likelihood of collisions with vanadium sites in the fly ash increases; therefore, the recovery rate of vanadium increases. The selected temperature in this research is 35 ℃ (This temperature was chosen when determining the preferred factors for this reaction to reduce the amount of energy consumed in heating the solution during the reaction. This temperature and close to it represent the temperature of aqueous solutions over long periods of the year in Baghdad , Iraq (especially between March and October), at which the vanadium recovery percentages are 66%, and 42% in case of presence, and absence of (0.1 M) TSC respectively [15].

Figure 6 shows the effect of time on vanadium recovery, where the percentage of vanadium recovery is 66%, and 42% in the presence, and absence of (TSC) at 12 hours. Beyond this time, the increase becomes minimal, reaching (67%, 43%) 24 hours. **Figure 7** shows the effect of increasing the solution ratio to the amount of fly ash on the increase in vanadium recovery percentage. The vanadium recovery percentage increases from 20% to 44%, and from 42% to 66% when the ratio of solutions to fly ash increases from 5 to

10 (whether in the absence or presence of TSC) due to the increase in carbonate and citrate ions in the solution. After that, the amount of increase is slight due to the binding of most vanadium sites to the ions.

Figure 8 shows the effect of the oxidizing agent on the increase in the recovery percentage of vanadium, which rises from (42%) to (57%) Potassium permanganate concentration (0.005M) without (TSC). The efficiency of vanadium recovery from its ores depends on providing ideal conditions for the oxidation of vanadium from (V^{+4}) to (V^{+5}). (V^{+5}) has lower solubility than (V^{+4}) , which facilitates the precipitation of vanadium from its solutions and increases its removal percentage. It is observed that TSC increases the vanadium recovery percentage in the presence of the oxidizing agent from (57%) to (85%).

Previous experiments show that the best conditions for recovering vanadium from fly ash using sodium carbonate and TSC solutions are as follows: sodium carbonate and TSC concentrations of (1, 0.1 M) respectively. Time = 12 hours. The ratio of solution to fly ash = 10. Potassium permanganate concentration = 0.005 M. Temperature= 35 ℃ (chosen to reduce energy consumption). It was found that the recovery rate of vanadium increased from (57% to 85%) when using TSC with sodium carbonate and oxidizing agent.

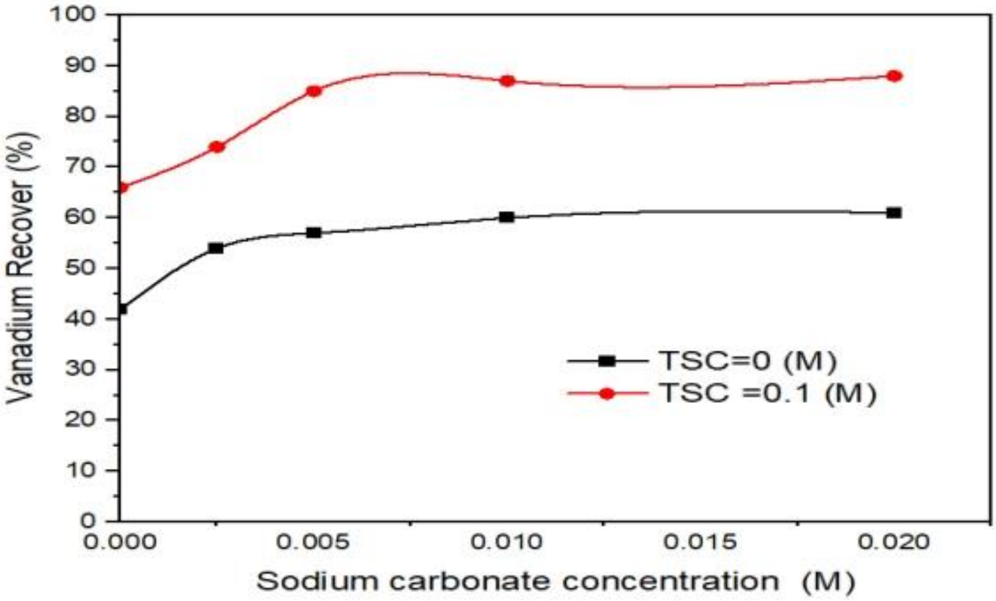

Figure 3. Effect of Na_2CO_3 concentration on vanadium recovery at 35 °C, leaching time is 12 hr., L/S is 10, and free $KMnO_4$

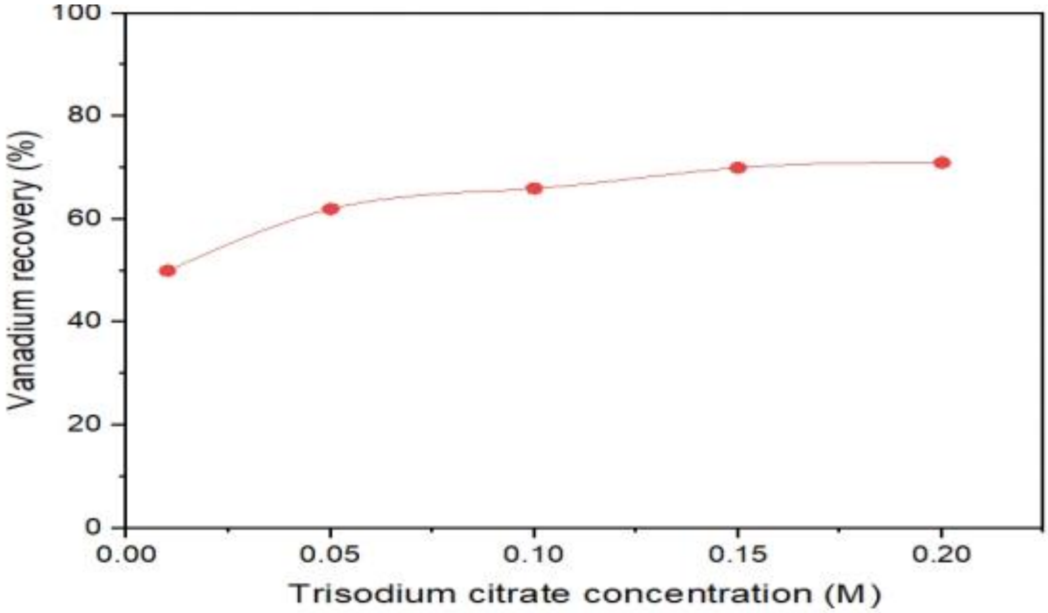

Figure 4. Effect of TSC concentration on vanadium recovery at 35°C, leaching time 12hr, L/S=10, free $KMnO_4$, and Na_2CO_3=1M

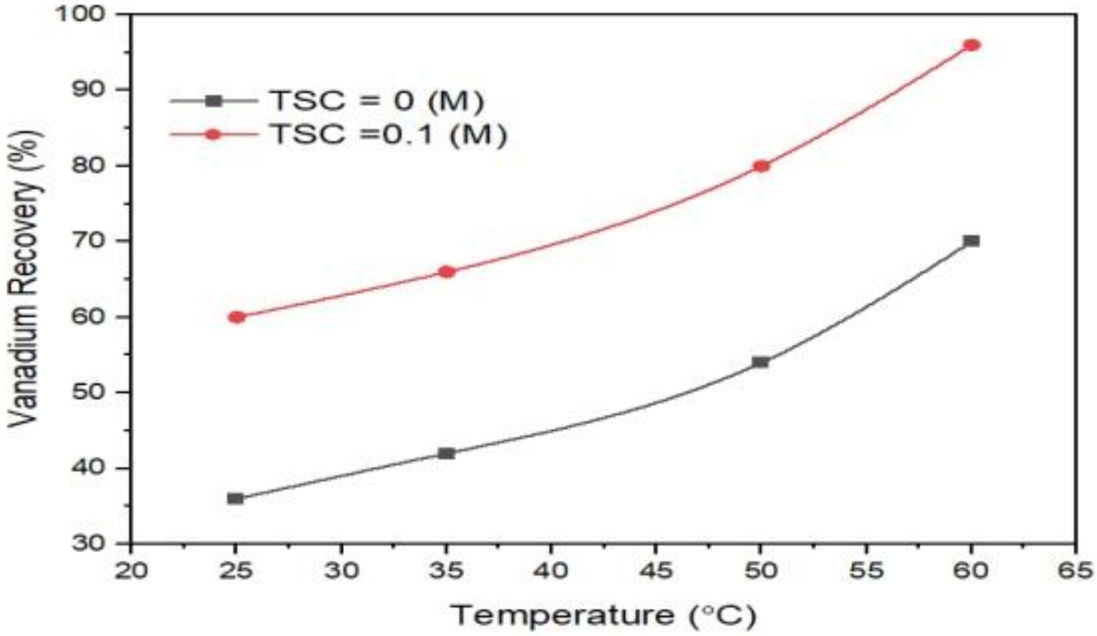

Figure 5. Impact of temperature on vanadium recovery at leaching time 12 hr., L/S =10, 1 M Na_2CO_3 , and free $KMnO_4$

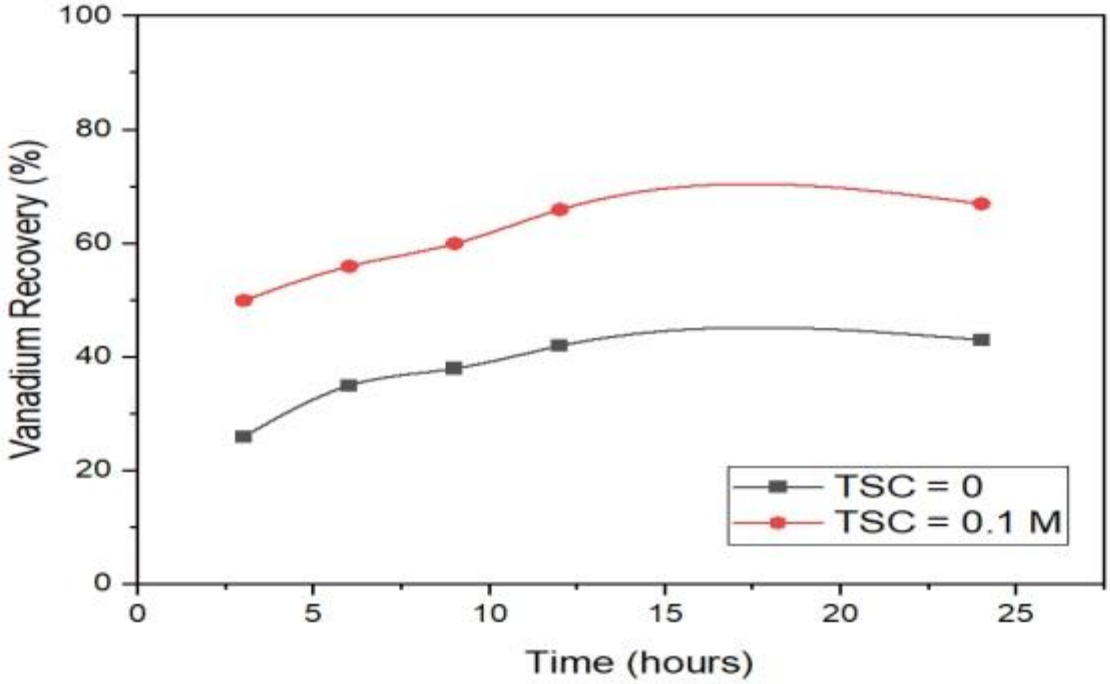

Figure 6. Impact of leaching time on vanadium recovery at 35 °C , L/S = 10, 1 M Na_2CO_3 , and free $KMnO_4$.

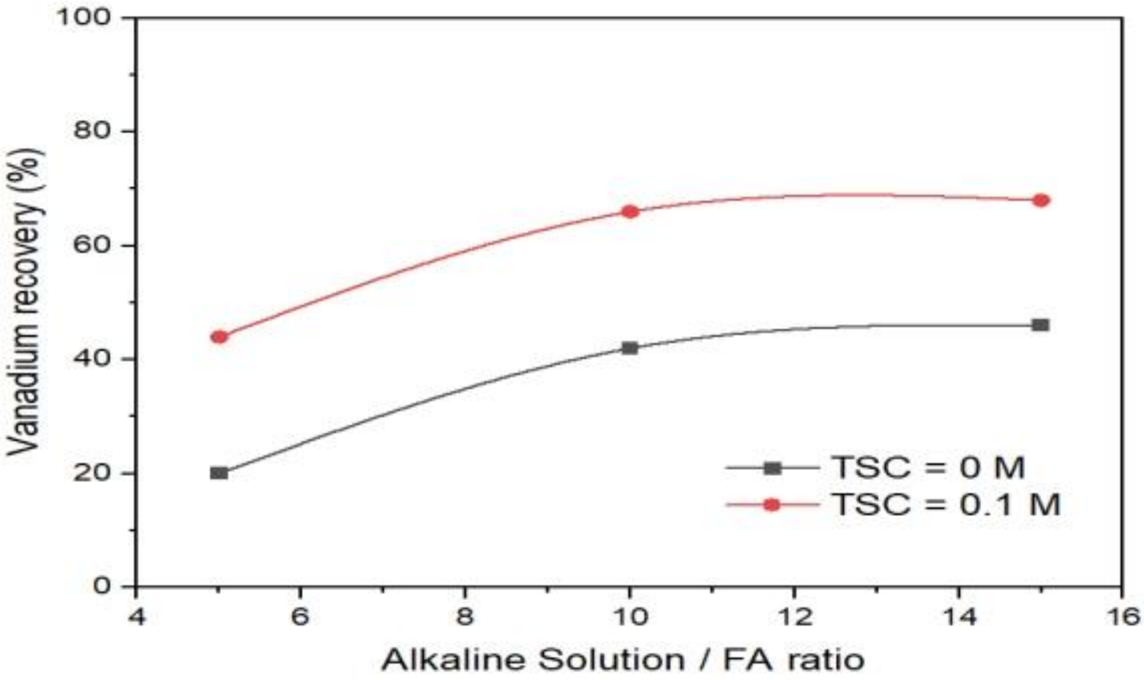

Figure 7. Effect of L/S ration on vanadium recovery at 35 °C, leaching time 12 hr., 1 M Na_2CO_3 , and free $KMnO_4$

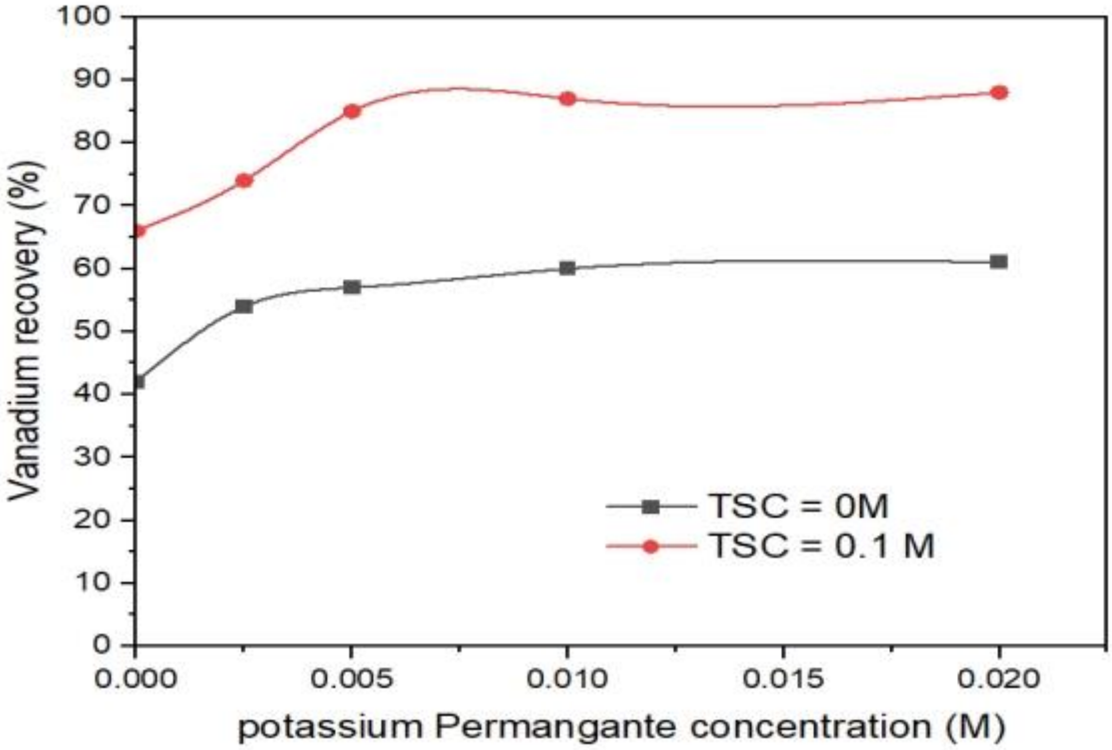

Figure 8. Effect KMnO4 concentration on vanadium recovery at 35°C, leaching time 12hr, L/S=10, and Na_2CO_3=1M

3.3. Vanadium precipitation

The solution was filtered after treating the fly ash with sodium carbonate and (TSC). After separating the precipitated materials, the pH of the filtrate was adjusted to 7 by adding nitric acid with continuous mixing to ensure the precipitation of most of the aluminum from the solution. The solution was filtered to remove the precipitated aluminum. 1 M Ammonium chloride solution was added to the resulting filtrate until the pH of the filtration reached 5. The filtrate was heated to 50 ℃ with continuous mixing for 6 hours, during which 85%

of the vanadium present in the filtrate will precipitate in the form of (AMV). The precipitate (AMV) was separated, washed with distilled water, and then dried at a temperature of 120 ℃ for 2 hours. (AMV) is roasted in a furnace at a temperature of 650 ℃ for 2 hours to obtain vanadium pentoxide with a weight percentage of 76%. The inverse weight percentage was used to calculate the purity of vanadium pentoxide. **Figure 9** and **Table 2**, which illustrate the percentage of the main elements in vanadium pentoxide produced after roasting.

Table 2. Main element in vanadium pentoxide

Element	C	O	Al	Si	S	V	Fe	Cu
Weight%	14.4	39.7	1	<0.1	0.3	42.5	<0.1	0.5

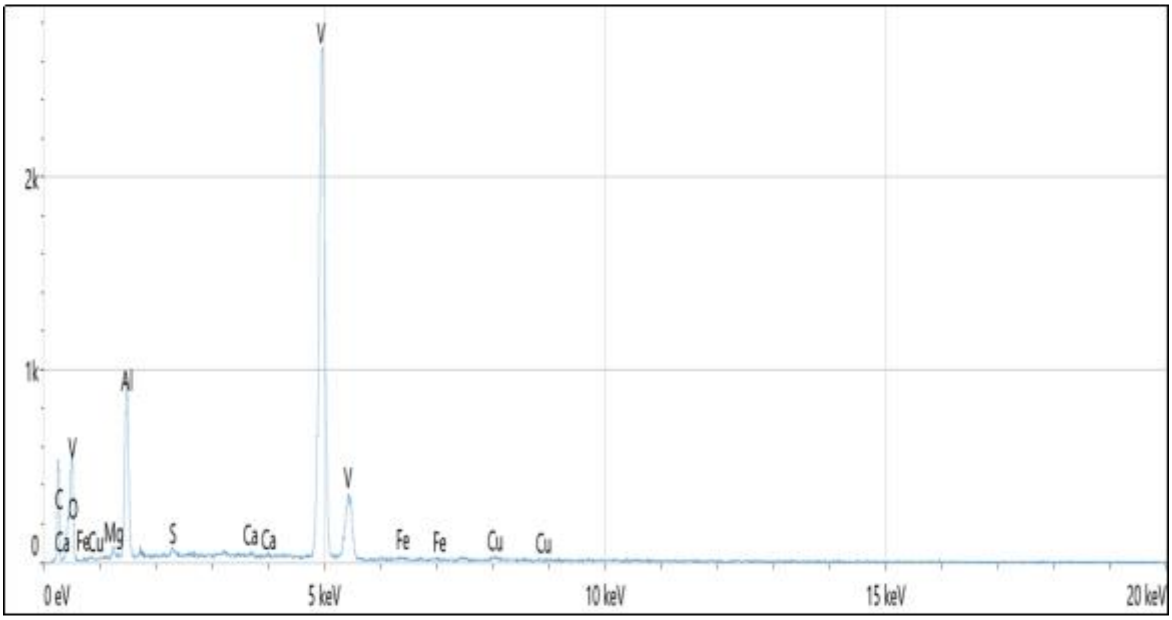

Figure 9. EDX of vanadium pentoxide produced

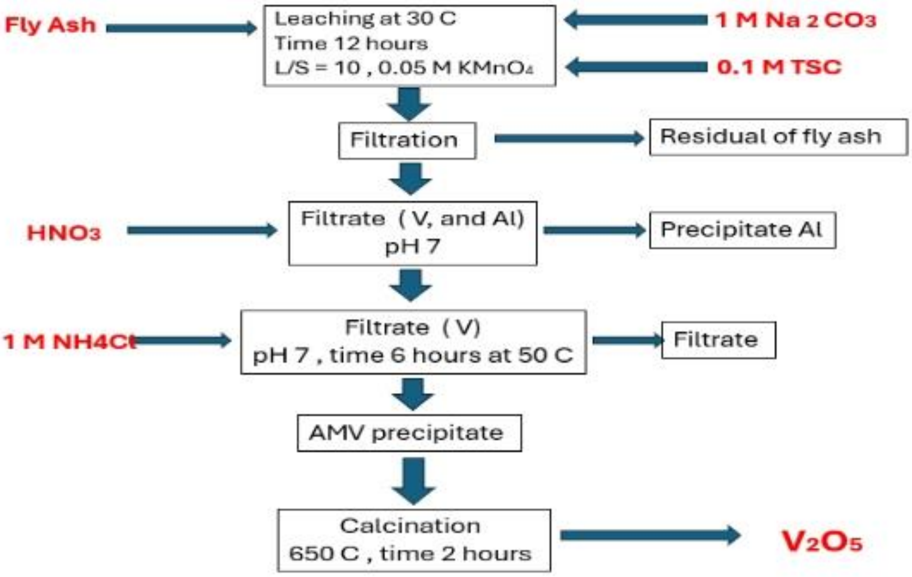

Figure 10. Flow diagram for the recovery of vanadium from fly ash using sodium carbonate solution in the presence of (TSC)

3.4. Kinetics of vanadium leaching

The reaction of fly ash with sodium carbonate and TSC solutions is classified as a heterogeneous reaction and is expressed by the unreacted-core model. The two main steps that control this model are the diffusion of ions through the ash blanket and the chemical reaction of ions with vanadium ore on the surface of the fly ash [26]. As shown in the equations.

$$K_d t=1+2(1-x)-3(1-x)^{\frac{2}{3}} \qquad \textit{controlled diffusion step} \qquad (3)$$

$$K_r t=1-3(1-x)^{\frac{1}{3}} \qquad \textit{controlled chemical reaction step} \qquad (4)$$

Where (x) represents the percentage of vanadium recovery, K_d is the diffusion rate constant, K_r is the vanadium chemical reaction rate constant and (t) represents the reaction time. The value of R^2 in **Figure 11, and 12** are 98%, and 91% respectively. This indicates that the control step of the reaction is the step of ion chemical reaction with vanadium ore.

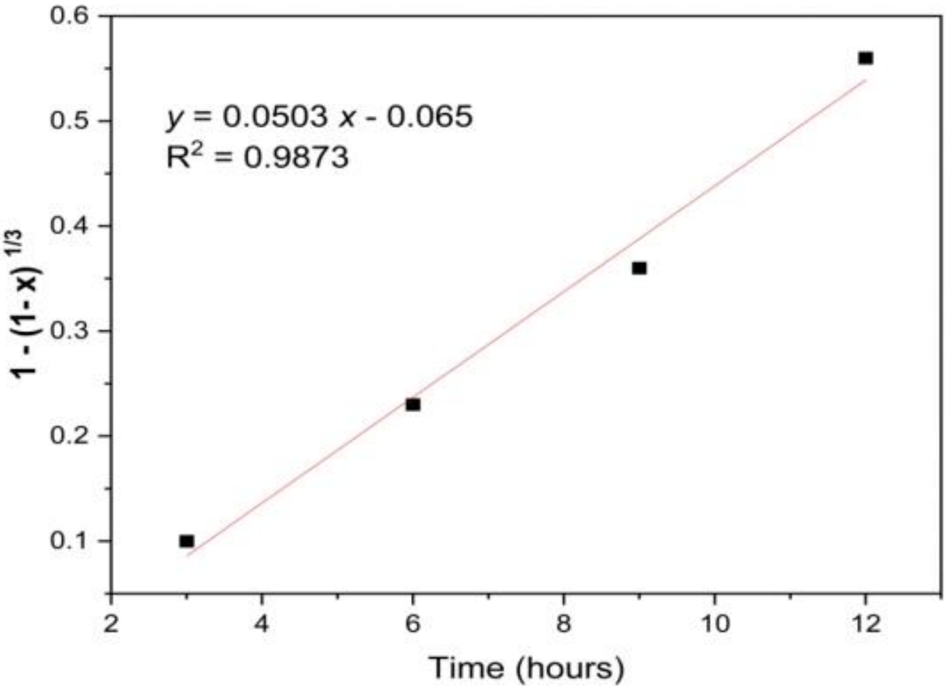

Figure 11. Un-reacted core model with reaction control

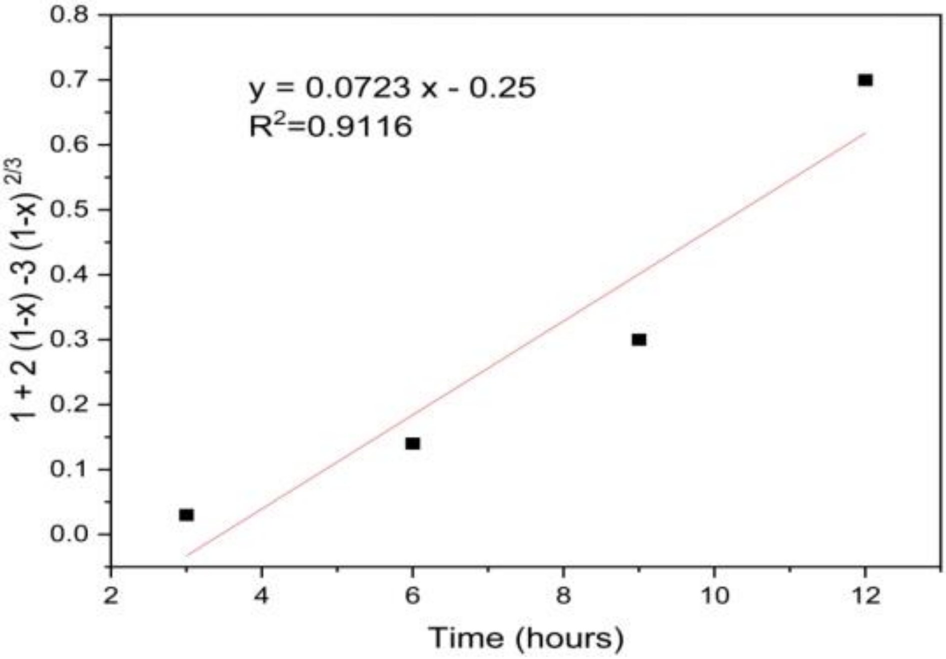

Figure 12. Un-reacted core model with diffusion control

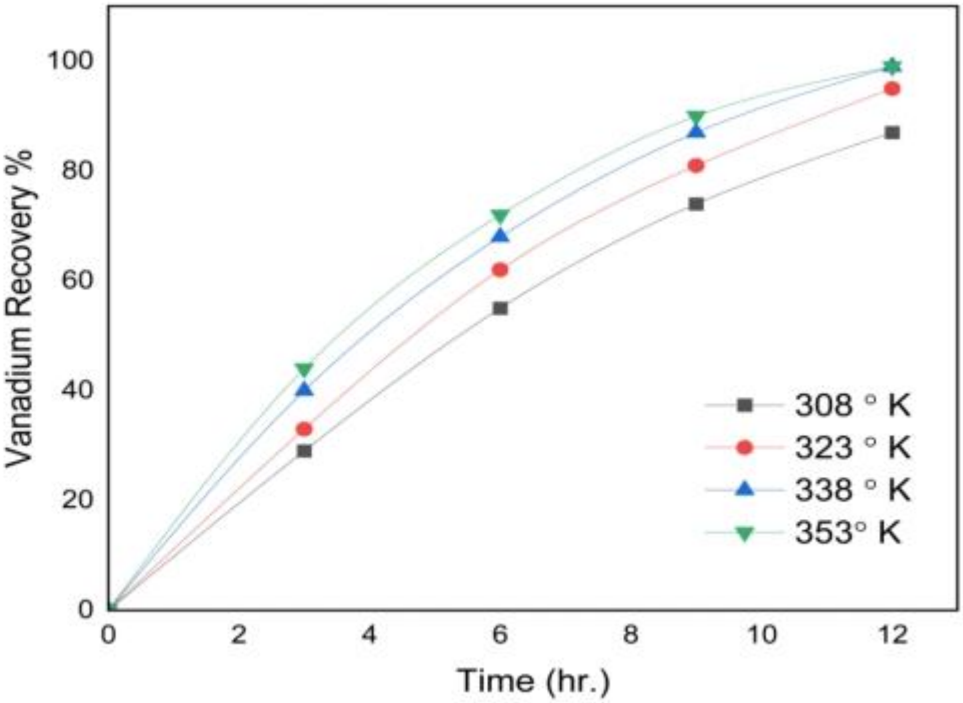

Figure 13. Effect of temperature on recovery vanadium from fly ash at (Na_2CO_3 (1M), TSC (0.1M), $KMnO_4$(0.005M), S/L(10))

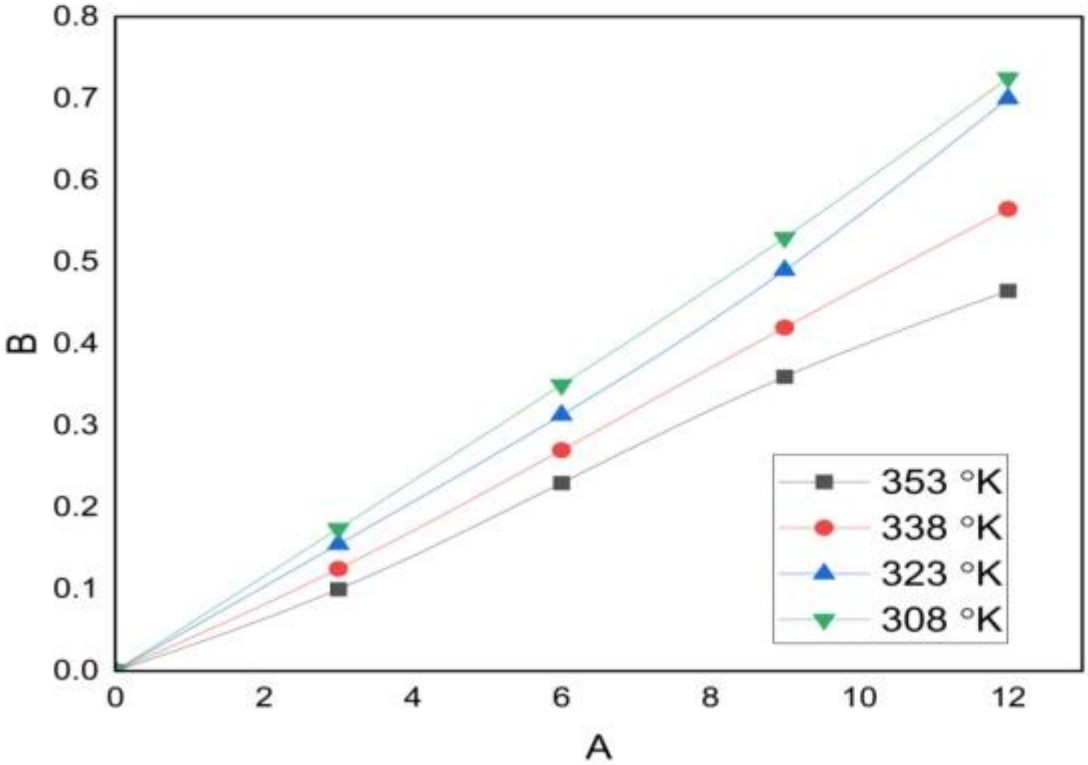

Figure 14. Relationship between time and $(1-(1-X)^{1/3})$ at (Na_2CO_3 (1M),TSC(0.1M), $KMnO_4$(0.005M), S/L(10)

The activation energy for the reaction is calculated using the Arrhenius equation [27-28]:

$$k=Ae^{\left(\frac{E_a}{RT}\right)} \rightarrow \ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

by plotting the relationship between ln(K) and (1/T) (**Figure 13,14,15**), where its value was found to be 8.47KJ/mol.

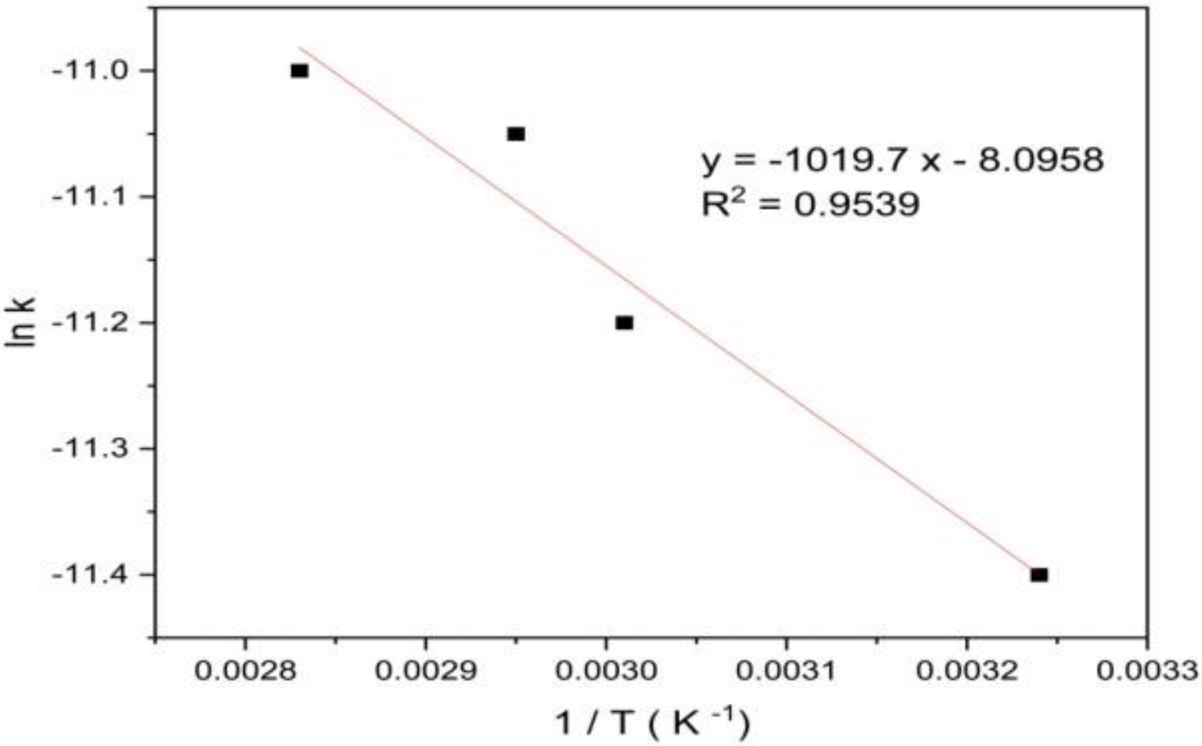

Figure 15. Arrhenius plot of ln(K) vs. 1/T for vanadium recovery reaction

4. Conclusions

The addition of tri sodium citrate to sodium carbonate solution in the presence of $KMnO_4$, significantly enhances vanadium recovery from (57%) to (85%). The factors affecting the recovery of vanadium are a time of 12 hrs, 1M sodium carbonate of ,0.1 M tri sodium citrate, 0.005 M potassium permanganate, and a liquid-to-solid ratio of L/S is 10. The temperature of 35 ℃, representative of natural ambient temperature in Iraq, was selected to minimize energy consumption. Vanadium was precipitated in the form of ammonium meta vanadate (AMV) by reacting it with ammonium chloride, which is converted to vanadium pentoxide with a purity of 76 % by roasting it at 650 ℃ and 2hours. When studying the kinetics of the reaction, it was found that the rate-controlling step of the reaction is the chemical reaction rate on the surface of the fly ash for the unreacted-core model, and the activation energy of the reaction (8.34KJ/mol).

Conflict of interest

The authors declare no conflict of interest.

References

1. Lee J.-C. Kurniawan E.-Y.K. Chung K. W. Kim R. Jeon H.-S. A review on the metallurgical recycling of vanadium from slags: towards a sustainable vanadium production. *J. Mater. Res. Technol*. 2021;12:343-364. https://doi.org/10.1016/j.jmrt.2021.02.065.
2. Nasimifar A. Mehrabani J. A review on the extraction of vanadium pentoxide from primary, secondary, and co-product sources. *Int. J. Min. Geol. Eng.* 2022;56(4):361-382. https://doi.org/10.22059/ijmge.2022.319012.594893.
3. Simandl G. J. Paradis S. Vanadium as a critical material: economic geology with emphasis on market and the main deposit types. Appl. Earth Sci.
4. Meawad, A. S., ojinova, D. Y. and Pelovski, Y. G., An overview of metals recovery from thermal power plant solid wastes. Waste Manage. 2010;30:2548. https://doi.org/10.1016/j.wasman.2010.07.010.

5. Imtiaz, M., Rizwan, M. S., Xiong, S., Li, H., Ashraf, M., Shahzad, S. M., & Tu,S. Vanadium: recent advancements, and research prospects: a review. Environment International, 2015;80:79-88. https://doi.org/10.1016/j.envint.2015.03.018.
6. Bafghi, M. Sh., Feiz, F. Sakaki, M. A parametric study on the sulfuric acid leaching of vanadium of an Iranian thermal power plant ash. Iranian Journal of Materials Science & Engineering. 2014;11(1):46-52.
7. Al-Ghouti ,M. A. Al-Degs, Y. S. Gharir, A. Koury, H. Ziedan, M. Extraction and separation of vanadium and nickel from fly ash produced in heavy fuel power plants. Chem. Eng. J. 2011;173:191-197. https://doi.org/10.1016/j.cej.2011.07.080.
8. LI Cun-xiong; et. al. Recovery of vanadium from black shale. Trans. Nonferrous Met. Soc. China. 2010;(20):s127-s131. https://doi.org/10.1016/S1003-6326(10)60026-X.
9. Deg Zhi-gan; et.al. Extracting vanadium from stone-coal by oxygen pressure acid leaching and solvent extraction. Trans. Nonferrous Met. Soc. China. 2010;(20):s118-s127.
10. El-Nadi; Y. A. Awwad; N. S. Nayl; A.A. A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst. Int. J. Miner. Process. 2009;(90):115-120. https://doi.org/10.1016/j.minpro.2009.03.005.
11. Alshaaer; M. Shqair; M. Adelwahed; H. G. Abuhasel; K. Toro; M. Z. Stabilization of heavy oil fly ash (HFO) for construction and environmental purposes. Int. J. Appl. Eng. Res. 2017;12(4):488-497.
12. Alamro T. Assessment of compression ignition engine's performance and emissive attributes powered with hybrid bio fuels. J. Umm. Al-Qura Univ. Eng Archit. 2021;12(2):1-6.
13. Al-Malack M. H. Bukhari A. A. Al-Amoudi O.S. Al-Muhanna H. H. Zaidi T. Characteristics of fly ash produced at power and water desalination plants firing fuel oil. Int. J. Environ. Res. 2013;7(2):455-466.
14. Hameed A. M. An eco-friendly ultrasound-assisted deep eutectic solvent-based liquid-phase micro extraction method for enrichment and quantification of nickel in environmental samples. J. Umm Al-Qura Univ. Appl. Sci. 2022;8:57-68. https://doi.org/10.1007/s43994-022-00009-2 .
15. Navarro R. Guzman J. Saucedo I. Revilla J. Guibal E. Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. *Waste Manag.* 2007;27(3):425-438. https://doi.org/10.1016/j.wasman.2006.02.002.
16. Barik S. P. Park K. H. Nam C .W. Process development for recovery of vanadium and nickel from an industrial solid waste by a leaching solvent extraction technique. J. Environ. Manag. 2014;146:22-28. https://doi.org/10.1016/j.jenvman.2014.06.032.
17. Stas J. Dahdouh A. Al-chayah O. Recovery of vanadium, nickel and molybdenum from fly ash of heavy oil-fired electrical power station. Chem. Eng. 2007;51(2):67-70. https://doi.org/10.3311/pp.ch.2007-2.11.
18. Hakimi M. Kiani P.T. Alikhani M. Feizi N. Bajestani A. M. Alimard P. Reducing environmental pollution offuel fly ash by extraction and removal vanadium pentoxide. Soild Fuel Chem. 2020;54(5):337-342. https://doi.org/10.3103/S0361521920050055 .
19. Jung M. Mishra B. Vanadium recovery from oil fly ash by carbon removal and roast-leach process. JOM. 2018;70:168-172. https://doi.org/10.1007/s11837-017-2653-7 .
20. Suanon F. Sun Q. Dimon B. Mama D. Yu CH. Heavy metal removal from sludge with organic chelators: Comarative study of N,N-bis(carboxymethyl) glutamic acid and citric. Journal of Environmental Management. 2016;166:341-347. https://doi.org/10.1016/j.jenvman.2015.10.035.
21. Rasoulnia P. Mousavi S. M. Rastegar S. O. Azargoshas H. Fungal leaching of valuable metals from a power plant residual ash using Penicillium simplicissimum: Evaluation of thermal pretreatment and different bioleaching methods. Waste Manag. 2016;52:309-317. https://doi.org/10.1016/j.wasman.2016.04.004.
22. Tsai S. L. Tsai M. S. A study of the extraction of vanadium and nickel in oil-fired fly ash. Resour. Conserv. Recycl. 1998;22(3-4):163-176. https://doi.org/10.1016/S0921-3449(98)00007-X.
23. Liu, Huidong, Qi Sun, Baodong Wang, Peipei Wang, and Jianhua Zou. 2016. "Morphology and Composition of Microspheres in Fly Ash from the Luohuang Power Plant, Chongqing, Southwestern China" Minerals 6, no. 2: 30. https://doi.org/10.3390/min6020030.
24. Heng, K. Y., T. Y. Kei, K. J. Singh, L. I. Hairui, P. O. H. Ai-Ling, and K. Lifeng. Handbook of cosmeceutical excipients and their safeties. Elsevier, 2014 , pp 275. https://doi.org/10.1533/9781908818713.75 .
25. (Baritto, M., A. O. Oni, and A. Kumar. Vanadium recovery from oil sands petcoke fly ash: A comprehensive techno-economic assessment. Waste Management 194 (2025): 249-257. https://doi.org/10.1016/j.wasman.2025.01.018.
26. O. Levenspiel, Chemical Reaction Engineering, Wiley New York, 3rd, 1998.
27. Alwan, H. H., Ali, A. A., Makki, H. F. (2020). Optimization of Oxidative Desulfurization Reaction with Fe2O3 Catalyst Supported on Graphene Box-Behnken Experimental Method. Bulletin of Chemical Reaction Engineering & Catalysis, 15 (1), 175-185 . https://doi.org/10.9767/bcrec.15.1.6670.175-185.
28. Mohammed, Israa, Hameed Hussein Alwan, and A. N. Ghanim. Study reaction kinetics of fuel model desulfurization by electrochemical oxidation technique.Al-Qadisiyah. J. Eng. Sci. 14 (2021): 001-005. https://doi.org/10.30772/qjes.v13i3.710 .