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Adsorption of thiocyanate from aqueous solution on the Ion exchange resin loaded AgCl as a hybrid selective resin

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Abstract—In this study, the ion exchanger resin was hybridized to the selective resin in the form of R-AgCl (SCR). The SCR was used as a chemical adsorbent of thiocyanate from aqueous solutions. The effect of several factors on the efficiency of hybrid resin SCR in batch system has been studied.

The factors were studied to obtain the optimal method of the adsorption process, the experiments were conducted with different of ; pH value, contact time, mass of SCR and the concentration of SCN^- was also varied between 1.0 mgL^{-1} to 50 mgL^{-1}, while the experiments were investigated at temperature of 25 °C to 40 °C.

The results showed that the adsorption process of SCN^- on SCR is significantly affected by pH value and the concentration of SCN^-, it was observed that the adsorption capacity increased in the acidic solution at pH value of (pH 4.0, pH 5.0 and pH 6.0) it was found that the capacity of adsorption is reached up to 95.8% at temperature 25 °C.

Keywords— thiocyanate, hybrid resin, AgCl, adsorption, aqueous solution, pH value

INTRODUCTION

Thiocyanate ion (SCN^-) enters to the environmental from several sources of industrial activities such as printing, coal, mining and textile dyeing [1,2,3], and reaches also via rodenticides and herbicides [2].

Thiocyanate is less dangerous than cyanide but it needs a long period time to hydrolyze [4] the toxicity of thiocyanate increases with decreasing of pH value, it has a harmful effect on human body [5].

Several techniques were used for adsorbing and removal of thiocyanate from aqueous solution the all methods were seeking for simple and easy method , among of these techniques are adsorption of thiocyanate on ferrihydrate [6], denitritation of thiocyanate which was effective method for removing thiocyanate from wastewater [7] , also nanoparticles metals were used as a good techniques for adsorption and removing of SCN^- , more than 108 mg g^{-1} of thiocyanate was removed by Nano-silver chloride loaded on hydrotalcite [8].

Some studies have utilized biodegradation technology in the aerobic and anaerobic system in the alkaline medium [9, 10]. Whereas good results were obtained by using two strains of the genus (Halomonas or Thiobacillus) to degrade thiocyanate [11], reliable results were also achieved by using the phytoremediation technique [12].

The techniques were varied, some studies confirmed that the ion exchange method had high sorption affinity towards thiocyanate reached to 98.3 mg g^{-1} and 191.2 mg g^{-1} respectively [13,14]

The Bio-film technical reactor is one of the methods that have been developed by the researchers to remove thiocyanate, the removal reached to more than 94% [15,16,17]. The variety methods was good and desirable, microbial is one of the most procedural for removing of thiocyanate by using metabolic division [18,19].

Many researchers were developed the by-product materials as a beneficial option for removing toxicity, due to cheapen, one of these studies used activated coir fiber by cztion surfactant hexadecyltrimethlammonium to remove thiocyanate[20]. While material such as Hydrotalcite, sepiolite, diatomite, zeolite and activated carbon were used as commercial materials for uptake the thiocyanate [1], however a good results have been observed by using zinc chloride loaded on activated carbon, the adsorption capacity reached to 16.2 mg g^{-1} [21], while straw as a cheap material supported ion imprinted polymer was used the study obtaind a very rapid adsorption equilibrium at pH 2.0 [22].

Adsorption and removal techniques are different and varied; some studies used expensive technique whereas others used cheap sorbent materials.

In this study seeking of developing a good adsorbent material by using anion exchange resin loaded with silver chloride (SCR) which is prepared in our laboratory according to [23] in order to selective adsorbed thiocyanate. A simple scheme of the chemical sorption of thiocyanate on the SCR is shown in figure 1

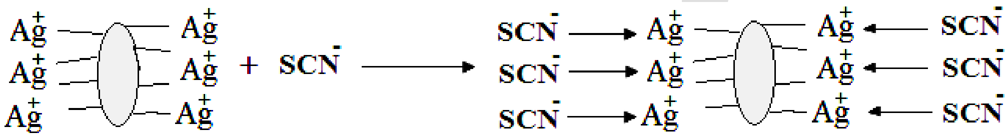

Figure 1.Scheme of the adsorbent of thiocyanate on SCR.

MATERIALS AND METHODS

Materials

All chemical used in this research were reagents grade: KSCN (BDH); $AgNO_3$ p.a (Riedel-de Haen) ; NaOH p.a (Merck); HNO_3 p.a (Merck); Lewatit MonoPlus M500, (Lanxess)

Thiocyanate

A stock solution of thiocyanate (1000 mgL^{-1}) was prepared by dissolving 1.672 g of potassium thiocyanate KSCN in 1000 mL of deionized water.

Method for determination of thiocyanate

The concentration of thiocyanate was spectrophotometric analyzed by using (320 D spectrophotometer at 480 nm with 10 mm quartz cell following ferric method.

Sorption process (SCR)

The SCR selective resin for adsorption thiocyanate was prepared according to [23]. The adsorption efficiency of the SCR towards thiocyanate was explored by batch system experiments ; the mass of SCR was varied from (0.25g – 3.0g) was weighed in 500 mL glass beaker connected with varied concentration of thiocyanate with range (1.0 mgL^{-1} - 50 mgL^{-1}) of 100 mL solution, a shaker speed at different temperature (25 C° , 30 C°, 35 C°) was 150 rpm, the pH of solutions were connected with range (pH 4.0 to pH 10.0) and the contact time was varied for experiments (30 to 240 minutes).

RESULTS AND DISCUSSION

Effect of pH value

The effect of the pH value of solution was investigated, the experiments conditions were; concentration of SCN^- (50.0 mgL^{-1}) , volume of solution (v=100 mL), mass of SCR (m=1.0 g), temperature (25 °C), contact time (120 min), shaker speed (150 rpm) , temperature (25 °C) and pH value was varied (pH 4.0 to pH 10).

The results obtained that the adsorption capacity completely is affected by the pH value of the solution as shown in Figure 2. The adsorption of SCN^- approximately stable in acidic and neutral medium.

The adsorption recovery results were 96.8 %, 95.8 %, 94.2 % and 86.5 % for the pH value 4.0, 5.0, 6.0 and pH 7.0 respectively.

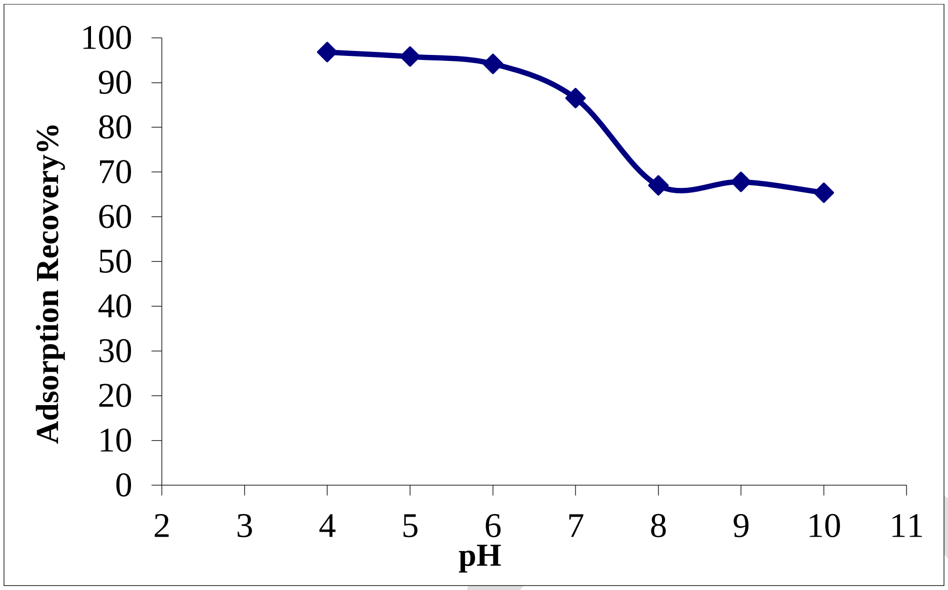

Figure 2. Effect of pH value on the adsorption of thiocyanate by SCR

While the adsorption capacity were decreased in the alkaline mediums , the recoveries were 67.0 %, 67.8 % , 65.4 % for pH value 8.0, 9.0 and pH 10 respectively it due to the fact that the SCR is modified with hydroxyl ions [24] by converted SCR to hydroxide AgOH. The effect of pH values showed that the highest adsorption capacities were in the acidic medium at pH 4.0 and pH 5.0, it recovered more than 96%.

Effect of contact time

The effect of contact time between SCR and SCN^- on the equilibrium sorption was studied at over time intervals of 30 min. to 240 min. The experiments for measuring the effect of contact time were as follows: concentration of SCN^- (50.0 mgL^{-1}), volume of solution (v=100 mL), mass of SCR (m=1.0g), temperature (25 °C), pH value (pH 5.0) , shaker speed (150 rpm) and contact time was varied (30 min. up to 240 min.). Figure 3 shows the adsorption capacity at different times, it has been noticed that the adsorption capacity at 60 min was acceptable it reached to 84.3 %, while at 120 min the adsorption was in the maximum it reached to 96.63%, however from 120 min. the adsorption capacity was approximately without change up to 240min.

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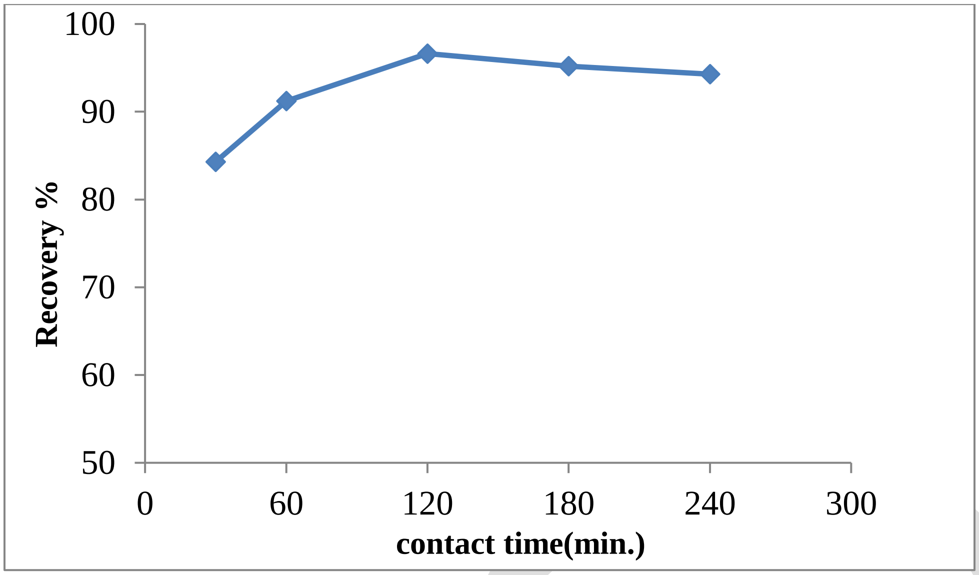

Figure 3. Effect of contact time on the adsorption of thiocyanate by SCR.

Effect of mass of SCR

The effect of different mass of SCR on the adsorption capacity has been studied. The experiments batch system were applied; mass of SCR was varied (m= 0.25 g to 3g) , pH value (pH 5.0), concentration off SCN^- (1.0 mgL^{-1}, 25 mgL^{-1} and 50 mgL^{-1}), volume of solution (v= 100 mL), contact time (120 min), shaker speed (150 rpm) and temperature (25 °C).

The experiments were conducted for purpose of determination the effect of the increasing the mass of SCR on the chemical adsorption of SCN^-, for each experiment the adsorption capacity was calculated.

The results obtained in figure 4 showed the following, by using weights of 0.25 g and 0.5g of SCR, the adsorption increased from 38% to 80% for all concentrations of SCN^- used in the experiments.

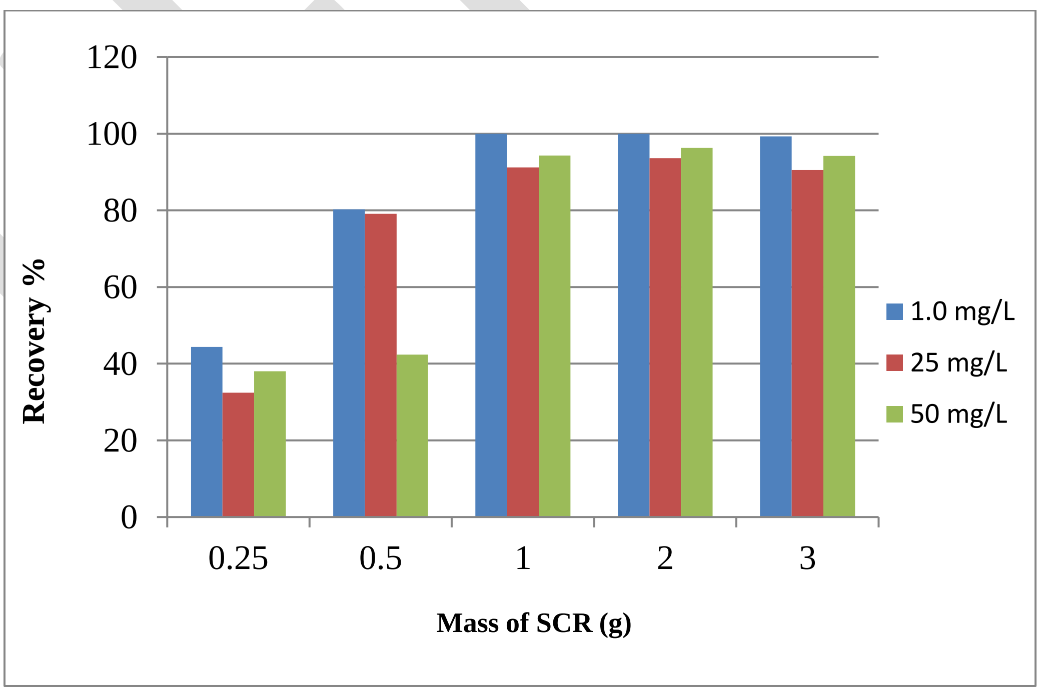

Figure 4. Effect of SCR doses on the adsorption of thiocyanate

At the same time , the results of the experiments used of SCR $\geq$ 1.0g , the adsorption recoveries for each concentration of SCN^- were approximately constant, it were 94.2% to 99.3% for 1.0g, 2.0g and 3.0g of SCR, it due to that the SCR has a high selectivity and ability to adsorption and removal high concentration of SCN^-.

Effect of temperature

The performance of hybrid resin SCR was studied at different temperature condition while the other factors were demonstrated constant, the experiments procedure were as a following; mass of SCR (2.0 g), pH value (pH 5.0), concentration of SCN^- (50 $mgL^{-1)}$, volume of solution (v= 100 mL), contact time (120 min), shaker speed (150rpm) and temperature was varied (25 °C to 40 °C).

The influence of temperature on the adsorption capacities were presented in figure 5. The results showed that the adsorption efficiency not affected by temperature of 25°C to 35°C, but there was clear effect on the performance of SCR at high temperature; the adsorption recovery was 71.8% at 40°C , the decreasing on the adsorption capacity due to dissociated of SCR.

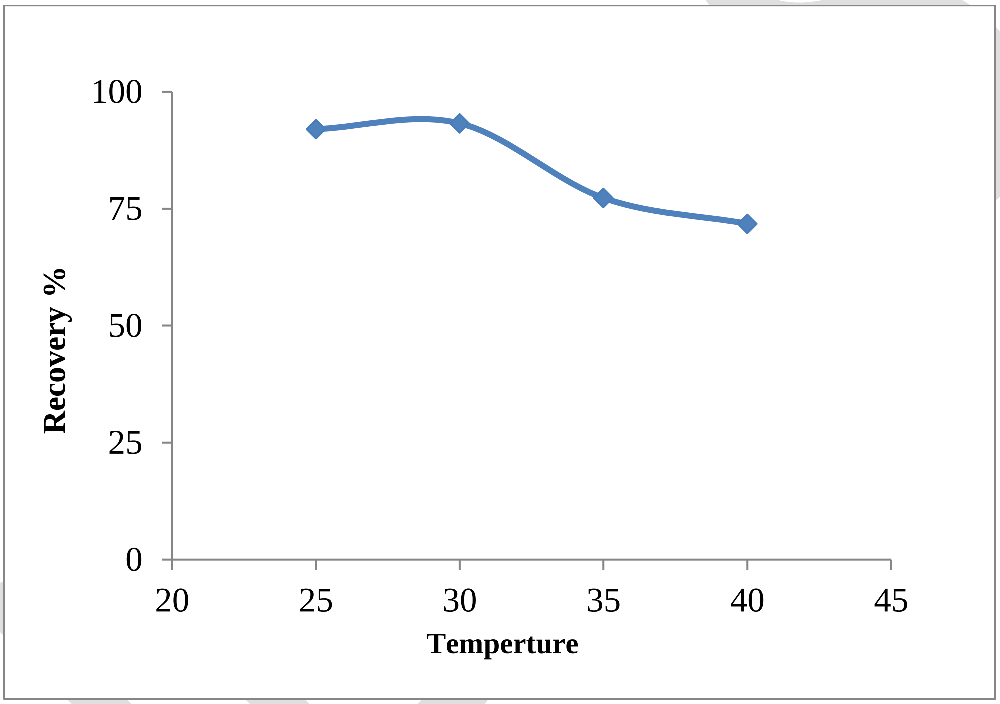

Figure 5. Effect of temperature on the adsorption of thiocyanate

Application on standard sample solutions

After studying the influence of all factors and fixing the optimal method, the experiments were carried out on standard solutions. Five sample of deionized water were spiked with different concentration of SCN^-, the optimum condition of experiment method was used as a following; mass of SCR (2.0 g), pH value (pH 5.0), spiked concentration of SCN^- (table 1), volume of solution (v= 100 mL), contact time (120 min), shaker speed (150rpm) and temperature was (25 °C).

Table1. The adsorption capacity of standard solution spiked with different concentration of SCN^-

Standard solution No.	Spiked solution SCN^- added, mg L^{-1}	SCN^- Adsorbed, mg L^{-1}	Recovery %
1	1.0	1.05±0.07	105
2	5.0	5.05±0.141	100.9
3	10.0	9.68± 0.18	96.83
4	25.0	23.83±0.65	95.32
5	30.0	28.9±0.52	96.33

The results in table 1, Showed that the adsorption of SCN^- for all samples was excellent and the recoveries of SCN^- were 105%, 100.9%, 96.83%, 95.32% and 96.33%, the relative standard deviation (RSD) of standard samples were 6.66% ,2.81%, 1.88%, 2.70 % and 1.79% for 1.0 , 5.0, 10.0, 25.0 and 30.0 mg L^{-1} respectively .

Effect of common ions present in water

Real water

Experiments were conducted on the two real water samples to evaluate the effect of common anions in water, the concentration of common ions in real water sample are presented in table 2.

Table 2. The concentration (mg L^{-1}) of selected anions in real water samples.

Sample	TDS	Cl^-	CO_3^{2-}	HCO_3^{3-}
A	897.7	210.2	ND	166.3
B	109	23.3	ND	29.3

The results of two real water samples were spiked with different concentration of thiocyanate are presented in table 3.
Although the salts adsorbed their ions, the results obtained in table 3 showed that there was no significant effect on adsorption of SCN^- in the presence of common ions due to chemisorption, the adsorption reached to 100% for low concentration of SCN^-, the recoveries adsorption were as follows ; 104% , 98.1 %, 93.2%, 95.07% and the relative standard deviation (RSD) of real two samples were 2.61%, 1.94%, 0.65% and 2.86% for 1A, 2A, 1B, and 2B respectively.

Table 3. Demonstrates of the adsorption results in real water samples spiked with different concentration of SCN^-

Sample No.	SCN^-, content added mg L^{-1}	SCN^-, adsorbed Mg L^{-1}	Recovery %
1A	5.0	5.20±0.13	104
2A	5.0	4.90±0.1	98.0
1B	10.0	9.32±0.06	93.2
2B	25.0	23.76±0.68	95.07

CONCLUSION

The results obtained from the experiments showed that the adsorption efficiency is greatly affected by pH value of solution and weight of SCR, where the adsorption increased by using weight between 1.0 g to 3.0 g. while the chemical reaction between SCR and SCN^- increased in acidic medium, the best adsorption capacity was achieved in the pH value (pH 4.0 and pH 5.0), while in the alkaline medium, the adsorption was obviously decreased.

The binding time was acceptable between AgCl and SCN^- the time was 120 min. and the adsorption capacity reached to 97 %, while at 60 min. the adsorption capacity was 84%.

This study provides effective method for selective adsorption thiocyanate from aqueous solutions. Further developed should be carried out for application of removal and preconcentration of thiocyanate.

REFERENCES:

1. Aguirre N.V., Padilla B., Montes- Moran V. A. and Ania C. O., Adsorption of thiocyanate anions from aqueous solutions on to adsorbent of various origin, Adsorpt. Sci. Technol. Vol. 28 No. 8/9 (2010) 705-715
2. Douglas Gould W., King M., Mohapatra B. R., Cameron R. A, Kapoor. A. and Koren D. W., A critical review on destruction of thiocyanate in mining effluents, Miner. Eng. 34 (2012) 38-47.
3. Budaev S. L., Bbatoeva A. A., Tsbikova B. A., Khandarkhaeva M. S. and Assev D. G., Photochemical degradation of thiocyanate by sulfate radical-based advanced oxidation process using UVC KrC1- excilamp, J. Environ. Chem. Eng., 9:4 (2021) 105584.
4. Turan A., Keyikoglu R., Kobya M. and Khataee A., Degradation of thiocyanate by electrochemical oxidation in coke oven wastewater: Role of operative parameters and mechanistic study, Chemosphere, 255 (2020) 127014.
5. ChunJuan D., Qingye P. and Yan Xia W., Thiocyanate removal from coking wastewater through granular sludge, Adv. Mater. Res, 955-959 (2014) 2370-2373.
6. Phuc Vu H. and Moreau J. W., Thiocyanate adsorption on to ferrihydrite and its fate during ferrihydrite transformation to hematite and goethite, Chemosphere, 119 (2015) 987-993.
7. Pan J., Ma J., Wu H., Ren Y., Fu B. M. He, Zku S. and Wei C., Simultaneous removal of thiocyanate and nitrogen from wastewater by autotrophic denitritation process, Bioresour. Technol., 267 (2018) 30-37.
8. Xie F., Borowiec J. and Zhang J., Synthesis of AgCl nanoparticles-loaded hydrotalcite as highly efficient adsorbent for removal of thiocyanate, Chem. Eng. J. 223 (2013) 584-591.
9. Benny C. and Chakraborty S., Continuous removal of phenol, organics, thiocyanate and nitrogen in horizontal subsurface flow constructed wetland, *J. Water Process Eng,* 33 (2020) 101099.
10. Wang X., li B., Chen J., Cui S., liu k. and Han Q., Cyclic degradation of thiocyanate in cyanide barren solution by manganese oxides, Miner. Eng., 176 (2022) 107314.
11. Stott M. B., Franzmann P., Zappia L. R., Watling H. R., Quan L. P., Clark B. J., Hiuchin M. R., Miller P.C. and Williams T. L., Thiocyanate removal from saline CIP process water by a rotating biological contactor, with reuse of the water for bioleaching, Hydrometallurgy, 62 ;2 (2001) 93-105.
12. Jian-Jie G., Wang B., Li Z., Xu J., Fu X., Han H., Li-Juan W., Wen-Hui Z., yong-Dong D., Wang Y, G. Ze-Hao, Yong-sheng T., Ri-He P. and Quan-Hong Y., Metabolic engineering of Oryza sativa for complete biodegradation of thiocyanate, Sci. Total Environ., 820 (2022) 153283.
13. Tao W., Dejun S., yujiang L., Z. Hong and Fengjuan L., Thiocyanate removalfrom aqueous solution by synthetic hydrotalcite sol, J. Colloid Interface Sci., 355 (2011) 198-203.
14. Dizge N., Demirbas E. and Kobya M., Removal of thiocyanate from aqueous solution by ion exchange, J. Hazard. Mater., 166 : 2-3 (2009) 1367-1376.
15. Hui-qiang, L. Hong-jun, M. H. Du and Wang W., Removal of phenols, thiocyanate and ammonium from coal gasification wastewater using moving bed film reactor, Bioresour. Technol. 102: 7 (2011) 4667-4673.
16. Chun D. J., Qing P. Y. and Yan W. X., Thiocyanate removal from coking wastewater through granular sludge, Adv. Mater. Res., 955-959 (2014) 2370-2373.
17. Villemur R., Juteau P., Bougie V., Menard J. and Deziel E., Development of four-stage moving bed biofilm reactor train with a pre-denitrification, Bioresour. Technol., 181 (2015) 254-262.
18. Pan J., Ma J., Wu H., Chen b., Meiling H., Liao C. and Chaohai W., Application of metabolic division of labor in simultaneous removal of nitrogen and thiocyanate from wastewater, Water Res., 150 (2019) 216-224.
19. Usha Mary T. M. and Swaminathan M., Enhanced biodegradation of thiocyanate by immobilized of *Bacillus brevis,* j. Indian Chem. Soc. 99 :8 (2022) 100588.

20. Namasivayam C and Sureshkumar M. V., Modelling Thiocyanate adsorption on to surfactant modified coir pith, an agricultural solid waste Process, Saf. Environ. Prot. 85: 6 (2007) 521-525.
21. Namasivayam C. and Sangeetha D., Kinetic study of adsorption of thiocyanate onto $ZnCl_2$ activated carbon from coir pith an agricultural solid waste, Chemospher, 60 :11 (2005) 1616-1623.
22. Wang J., Han Y., Li J. and Wei J., Selective adsorption of thiocyanate anaions using straw supported ion imprinted polymer prepared by surface imprinting technique combined with RAFT polymerization, Sep. Purif. Technol.177 (2017) 62-70.
23. Ben Issa N., Rajakovic V., Marinkovic A., D., Rajakovic L.V., Separation and determination of arsenic species in water by selective exchange and hybrid resin, Anal. Chim Acta 706 (2011) 191-198.
24. Namasivayam C. and Pratgap K., Removal of thiocyanate by industrial solid wasre Fe (III)/Cr (III) hydroxide: kinetic and equilibrium studies, J. Environ. Eng, Mange. 16:4 (2006) 267-274.