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Column Studies for the Simultaneous Removal of Phenol, Ammonia and Thiocyanate by the Adsorption with Steel Slag

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***Abstract:** Continuous adsorption experiments are carried out in a fixed-bed to evaluate the performance of the steel slag for the removal of phenol, ammonia and thiocyanate. The effect bed height and flow rate on the breakthrough curve is studied. The study reveals, phenol adsorbed per gram of the steel slag is 0.44 to 1.23 mg/g, ammonia adsorbed per gram of steel slag is 0.85 to 1.96 mg/g and thiocyanate adsorbed per gram of the steel slag is 0.07 to 0.32 mg/g of steel slag. Kinetic models like Thomas and Yoon Nelson Model were applied to the studies. Thomas and Yoon Nelson Model fit well when the mass of adsorbent was less for removal of ammonia and phenol. However, in case of removal of thiocyanate, Thomas and Yoon Nelson Model fits well if the mass of adsorbent is high.*

***Keywords:** Column studies, phenol, ammonia, thiocyanate, steel slag*

I. INTRODUCTION

Adsorption studies are either by batch studies or by continuous flow/column studies. Most of the research is done in batch mode as it requires less adsorbent and less time. Batch studies provide information on the adsorption capacity of the adsorbent, kinetic and thermodynamic studies. Continuous flow system provides information on effect of bed height, large-scale wastewater volumes which help in determining performance of column bed with flow of wastewater. Kinetic models such as Thomas model and Yoon–Nelson model are mostly used in the column studies for modelling of breakthrough curves.

In the present studies adsorption of phenol, ammonia and thiocyanate are studied. Phenol, ammonia and thiocyanate co-exist in the coke-oven wastewater. Their presence in wastewater is harmful. High exposures to phenol may be fatal to human beings; infants appear to be hyper susceptible[1]. Ammoniamay cause eutrophication of surface water and is known to be toxic to all vertebrates causing neurological disorder, coma or even death[2]. Thiocyanate is less toxic however it is reported to affect the growth and reproductive system of the fish [3].

Rising trend of patenting in the area of adsorption shows that industries are relying on this technology for the treatment of wastewater[4][5]. The most usual adsorbents for water treatment are activated carbons(ACs)[6]. Other adsorbents reported in literature for the adsorption of phenol are Manganese/silicon tailing waste [7] olive mill waste [8][9], cereal by products[10],cherry stone [11], rice husk ash [12], tobacco Residue [13],acid treated slag [14], coking coal [15].Adsorption of ammonia is done by natural Australian zeolite [16],bentonite/chitosan beads [17], natural Chinese clinoptilolite[18], natural and NaCl-modified zeolites [19],Lime stone and granulated activated carbon[20], Canadian zeolite [21], modified polyurethanes using alginate [22]. Thiocyanate adsorption is done by the adsorbents like calcinedhydrotalcite[23], Fe(III)/Cr(III) hydroxide waste [24], surfactant-modified coir pith [25], synthetic hydrotalcite sol [26], ferrihydrite[24], AgCl nanoparticles-loaded hydrotalcite[27]. Most of the studies concluded that Langmuir and Freundlich describes isotherm and Pseudo second order model describes the kinetics of adsorption. It is also reported that presence of one pollutant in the wastewater effects the removal of other pollutant. Adsorption of phenol was found improved on the resin in the presence of ammonia [28]. Presence of thiocyanate is found to be affect the removal efficiency of phenol as well as ammonia [29].

Very few studies are focused on the use of industrial waste as an adsorbent. Most of the studies are focused on batch studies. Column studies provide the effect of bed height and performance of adsorbent under the continuous flow of wastewater. The aim of the study is to provide the performance of the steel slag as an adsorbent for the removal of phenol, ammonia and thiocyanate. Adsorbent used in these studies is a steel slag, the waste material from the steel industry. Piles of steel slag can be seen of the steel slag near the steel industries. Recently, steel slag has gained some commercial value and is known better for its use in as

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cementations material, aggregate in bituminous mixes, antiskid aggregate, ceramic ingredient, thermal insulator, railroad ballast, landfill daily cover material [30].

II. MATERIALS AND METHODS

Steel slag from Steel Authority of India Limited (SAIL), Bokaro, India is screened and the 150 microns retained size is selected for the purpose of experimentation. Slag is washed with distilled water and dried in an oven for 24 hours at the temp of 150^{o}C, then kept in a desiccator for further use. Glass columns of diameters 30 mm, 40 mm and 50 mm having one side open and other side having regulated flow is taken for the column studies. All columns are of 100 mm height. One pump, overhead tank and excess liquid tank are taken for the purpose of the column studies. Experimental setup is as shown in the Figure 1 wherein wastewater is first pumped to the overhead tank and waste water is passed to the column. Overflow if any of wastewater from the overhead tank is collected in the excess liquid tank. The column is first filled with glass wool then glass beads then slag of desired height then by glass beads and then glass wool.

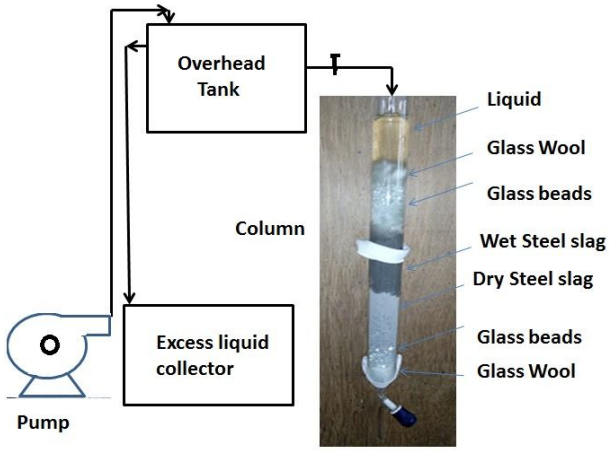


Figure 1: Experimental setup of the column studies

All the necessary chemicals used in the study were of analytical grade. AR grade Phenol, NH4Cl and Potassium Thiocyanate from (CDH (P) LTD) are used to prepare solutions of phenol, ammonia and thiocyanate. Distilled water is used for preparing solution. Concentration of phenol is determined by the use of direct photometric D1783-13408, ammonia is determined using phenate method [31] and thiocyanate is determined by iron (III) by measuring the intense red color[32].Concentration is determined by UV spectrophotometer (Milton Roy Company (USA), range 340-960 nm). The solution of phenol, ammonia and thiocyanate are mixed in equal proportion and has the concentration of 43 mg L^{-1} of phenol, 18 mg L^{-1} of ammonia and 32 mg L^{-1} of thiocyanate.

All experiments were performed in triplicate. The pH is measured with pH Meter, Japsin product, India. X-ray fluorescence is done by WDXRF Spectrometer - Bruker S4 PIONEER,USA. Scanning electron microscopy is obtained from Zeiss Model: V5:05 (SIGMA), Germany. X-ray diffraction is done [33]using Rigaku Smart lab Guidance CuKa irradiation (1.54 A0, 40 kV, 30 mA),Japan.

III. ADSORPTION STUDIES

Column studies are done to determine performance of steel slag on the adsorption of phenol, ammonia and thiocyanate. Experiments are done to investigate the effect of bed height, column diameter and the flow of the wastewater on the removal of toxicants.

Three columns of 30 mm, 40 mm and 50 mm diameter are taken for the adsorption studies. Adsorbent height in each column was varied to 50 mm, 100 mm and 150 mm. Similarly, the flow in each column was varied to 33.2, 38.5 and 43.8 mL min^{-1}.Breakthrough curve provides the information like, $t_{f,}$ (min) total time taken for the adsorption process; tb, (min) breakthrough time of the process. From the above the stoichiometric amount of toxicant adsorbed (q_t), the quantity of toxicant supplied to the column (m_t), exhaustion rate of adsorbent (Ra), the total percentage removal of toxicant (S), fraction of the unused bed length (y) and the EBRT are calculated and reported in Table 2, 3 and 4 which arehelpful for the column studies.The column studies are done based on the equations given below [34].

$q_{t,}$ mg is amount of pollutant adsorbed in column experiments is given by equation 1.A_c is the area under the curve which is representing adsorbed concentration C_{ad}, mg L^{-1} in time t, min.Q is flow rate during the process mL min^{-1}.

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$$q_t = {QA_c}/{1000} = {Q}/{1,000}\int_{t=0}^{t=t_{total}} C_{ad}\,d_t \quad (1)$$

$m_t$is amount of pollutant passed through the column and is given by equation 2.t_t,(min)is the time equivalent to the total stoichiometric capacity of fixed bed column and is given by equation 3.S, is percentage removal of toxicant as given in equation 4.EBRT is empty bed residence time which is the total time required to occupy the empty column and is given by equation 5.Ra is the Adsorbent exhaustion rate which indicates the amount of adsorbent required for unit volume of liquid till the breakthrough time and is given by equation 6.y is unused bed length and is given by equation 7.

$$m_t = {C_{bo}Qt_t}/{1,000} \quad (2)$$

$$t_t = {q_t t_f}/{m_t} \quad (3)$$

$$S = {q_t}/{m_t} \times 100 \quad (4)$$

$$EBRT = {Bed\ volumn}/{Volumetric\ flow\ rate} \quad (5)$$

$$R_a = {Mass\ of\ adsorbent\ in\ column}/{Volume\ treated\ at\ breakthrough} \quad (6)$$

$$y = 1 - {t_b}/{t_t} \quad (7)$$

IV. KINETIC STUDIES

Most of the kinetic studies determine the fitness of Thomas Model and The Yoon-Nelson model for column experiments. Thomas model is based on the assumption that rate of adsorption is second orderreversible reaction kinetics and the Langmuir isotherm. The linear zed form of the model is given by equation 8.

$$ln\left(\frac{C_0}{C_t} - 1\right) = \left(\frac{K_{Th}q_0 m}{Q}\right) - \left(\frac{K_{Th}q_0 V_{eff}}{Q}\right) \quad (8)$$

Where, q_o is the pollutant adsorbed per gram of the adsorbent (mg g-1), K_{Th} is the Thomas rate constant, and m is the amount of adsorbent in the column (g). K_{Th} and $q_o$is determined fromplot of ln((Co/Ct) -1) against t =Veff/Q) at a given flow rate.

Yoon-Nelson model is based on the assumption that rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorb ate adsorption and the probability of adsorbate breakthrough on the adsorbent. The linearized form of Yoon and Nelson model for a single component system is expressed by equation 9.

$$ln\left(\frac{C_t}{C_0 - C_t}\right) = K_{YN}t - \tau K_{YN} \quad (9)$$

Where, K_{YN} is the rate constant (min-1) and τ is the time required for 50 % adsorbate break through (min).The values of parameters KYN and τ for the adsorbate can be calculated from the plot ofln(Ct/(Co – Ct)) versus sampling time (t).

IV. RESULTS AND DISCUSSION

A. Steelmaking slag

The steel slag is a whitish dusty and the size of the grain varies from 0.75 microns to 4 mm in diameter. Sieve analysis is done and it shows that the steel slag is well graded. Table 1 shows the slag composition. Figure 2 shows the porous nature of the steel slag which indicates that abundance of adsorption sites on its surface.XRD of the steel slag reveals that it has $CaCO_3$, SiO_2, C_3S, C_2S as its main phases, however no distinct peaks are seen. This confirms that steel slag is amorphous in nature. The surface morphology of steel slag particle shows sharp edges, partly dense, and partly porous. The pore diameter, BET surface area, and the pore volume measured of the steel slagis4.06 nm, 11.6 m2/g, and 0.010 cc/g respectively. According to the IUPAC, the material can be classified as mesoporous material. This is also confirmed by the studies done elsewhere [35].

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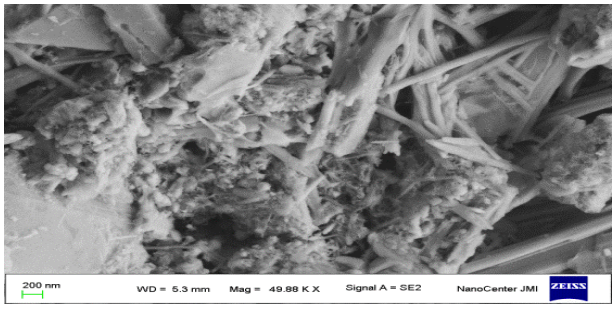


Figure 2: SEM of Steel Slag

Table 1: XRF of steel slag

Sample	Slag
CaO	46.21%
Fe_2O_3	14.89%
SiO_2	9.52%
MgO	2.51%
Al_2O_3	1.94%
P_2O_5	1.20%
TiO_2	0.56%
MnO	0.52%

B. Adsorption of phenol

Figure 3 shows that increase in bed height of the slag in the column increase the breakthrough time but increase in flow of wastewater in the column reduces the breakthrough time. In case of low bed height of 50 mm it was found that breakthrough time was too short and the bed height was ineffective for adsorption of any toxicant in the column studies. It is observed that breakthrough curve follows ideal "S" shape profile which is the characteristic of presence of small molecules of adsorbates and also small size particles of adsorbent [36].

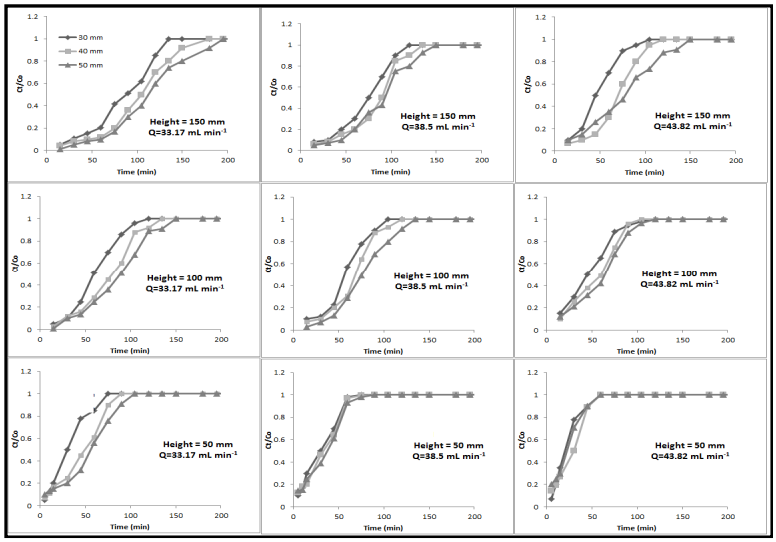


Figure 3: Breakthrough curves for Phenol adsorption

As the flow of wastewater is increased from 33.2 mL/min to 43.8 mL/min, the breakthrough time decreased from 45 to 25 min (Table 2). The total time required for the adsorption is analogous to the stoichiometric capacity of the column and is found to be

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decreased from 120 to 90 min when the inlet concentration and bed volume is constant. However, there is an increase in the fraction of the unused bed length from 0.49 to 0.65. The total percentage removal of phenol increased from 74 to 79.6 %, while the adsorbent exhaustion rate increases from 202.3 to 275.7 g L−1 with an increase in the flow of wastewater. The bed saturation and the breakthrough time are obtained earlier with an increase in the flow due to the relatively rapid rate of mass transfer. The decrease in the breakthrough time may be a result of faster saturation of slag as the more molecules of phenol and other toxicant present in the wastewater are available to saturate the active sites. Similar observation is found for the observations for the column of diameter 100 mm and 50 mm.

The effect of the mass of the adsorbent on the breakthrough curve is studied for variable mass that is 101, 179, 201, 280, 302, 358, 559, 537, 839 g depending on the bed height and column diameter. The other parameters such as the flow rate are maintained constant at 33.2, 38.5 and 43.8 mg L−1.

With an increase in the mass of the adsorbent from302 to 839 g with a flow of 33.2 mg L-1 the time acquired for breakthrough is increased from 45 to 60 min and the total time required corresponding to the stoichiometric capacity of the column increases from 120 to 180 min. The total percentage removal of the phenol decreased from 74.1 to 67.9 %, however, the fraction of the unused bed length and the adsorbent exhaustion rate increased from 0.49 to 0.51 and from 202.3 to421.5 g L−1, respectively, with an increase in the mass of the adsorbent from 302 to 839 g. The adsorbent exhaustion rate increase with an increase in mass of adsorbent which depicts that more the adsorbent better is the removal efficiency but increase in unused bed length suggests that slag is not fully utilised. Similar observation is found for other studies done with the same bed height but with different column diameter.

In the removal of phenol studies fraction of the unused bed length was higher at 50mm bed height and 43.8 mL/min and 179 g. Fraction of the unused bed length was minimum for 150 mm bed height and 537 g of slag with a flow of the wastewater at 33.2 mL/min. This shows that fraction of the unused bed length is affected by the bed height and flow.

Table 2: Different parameters for the measurement of phenol adsorption in column studies

Column Height	Q (mL/min)	W(g)	t_t (min)	t_f (min)	t_b (min)	q_t(mg)	m_t (mg)	S %	EBRT	Ra (g/L)	Y
150 mm	33.2	302	89	120	45	94	127	74.1	4.71	202.3	0.49
		537	98	150	60	92	140	65.6	7.07	269.8	0.39
		839	122	180	60	118	174	67.9	14.7	421.5	0.51
	38.5	302	71	105	35	80	118	68.0	4.71	224.1	0.51
		537	79	120	45	87	132	66.2	7.07	309.9	0.43
		839	92	135	45	103	152	68.0	14.7	484.3	0.51
	43.8	302	72	90	25	107	135	79.6	4.71	275.7	0.65
		537	74	105	30	97	139	70.1	7.07	408.4	0.59
		839	100	135	35	140	189	74.2	14.7	547.0	0.65
100 mm	33.2	201	78	105	15	83.5	111.9	74.7	0.9	404.7	0.81
		358	84	120	15	84.2	120.0	70.1	2.1	719.4	0.82
		559	94	135	15	92.9	133.7	69.5	5.9	1124.1	0.84
	38.5	201	65	90	30	78.2	108.0	72.5	0.8	174.3	0.54
		358	75	105	30	89.4	124.6	71.7	1.8	309.9	0.60
		559	84	120	30	96.8	138.7	69.8	5.1	484.3	0.64
	43.8	201	87	105	15	136.9	164.6	83.2	0.7	306.3	0.83
		358	68	90	15	95.8	127.5	75.2	1.6	544.6	0.78
		559	80	105	15	114.2	150.3	76.0	4.5	850.9	0.81
50 mm	33.2	101	50	60	15	60.1	71.7	83.8	0.5	202.3	0.70
		179	57	75	15	61.4	81.1	75.8	1.1	359.7	0.74
		280	68	90	10	73.0	96.8	75.4	3.0	843.1	0.85
	38.5	101	52	60	10	73.4	85.4	85.9	0.4	261.5	0.81

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		179	65	75	10	94.0	108.0	87.0	0.9	464.9	0.85
		280	79	90	10	115.6	131.2	88.1	2.5	726.4	0.87
	43.8	101	41	45	10	70.4	77.3	91.1	0.4	229.7	0.76
		179	38	45	5	61.0	71.9	84.8	0.8	816.9	0.87
		280	40	45	10	68.6	76.3	89.9	2.2	638.2	0.75

C. Adsorption of Ammonia

The observation on breakthrough curve for phenol is also found to be true for the breakthrough curve for adsorption of ammonia as shown in Figure 4. Less bed height is found to be ineffective towards column studies.

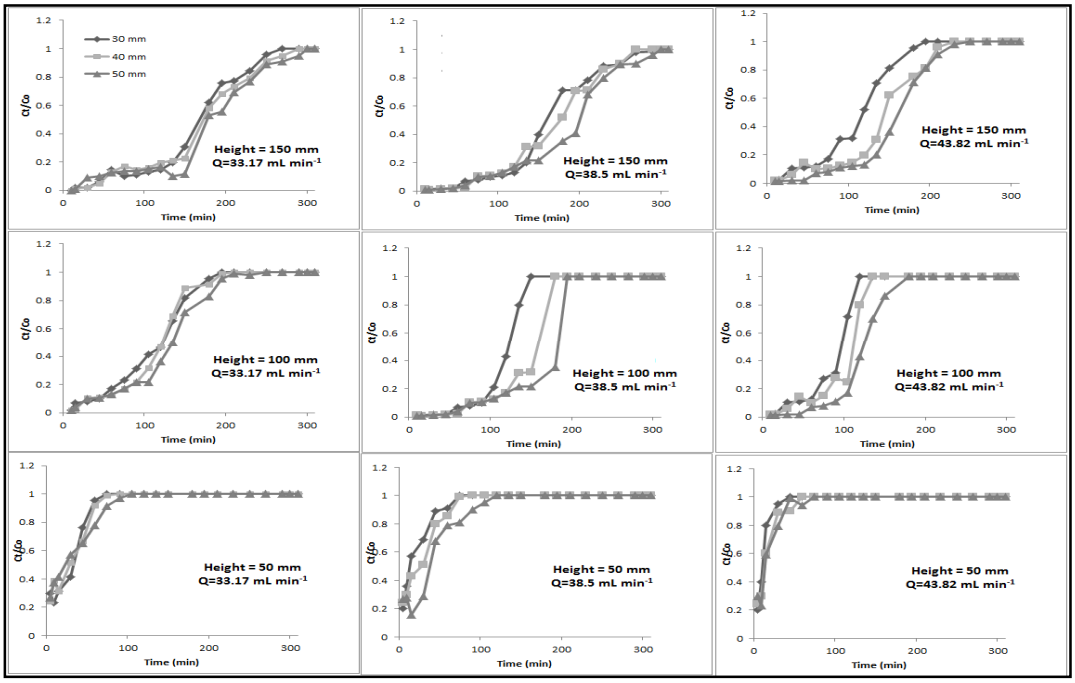


Figure 4: Breakthrough curves for ammonia adsorption

Table 3: Different parameters for the measurement of Ammonia adsorption in column studies

Column Height	Q (mL/min)	W(g)	t_t (min)	t_f (min)	t_b (min)	q_t(mg)	m_t (mg)	S %	EBRT	Ra (g/L)	Y
150 mm	33.2	302	162	250	110	63.0	96.9	65.0	1.4	82.8	0.32
		537	169	270	125	63.3	101.0	62.6	3.2	129.5	0.26
		839	172	290	125	60.8	102.6	59.3	8.9	202.3	0.27
	38.5	302	183	290	110	80.2	127.0	63.2	1.2	71.3	0.40
		537	158	250	110	69.5	109.7	63.3	2.8	126.8	0.31
		839	146	250	105	59.4	101.5	58.6	7.6	207.5	0.28
	43.8	302	122	180	80	65.5	96.4	67.9	1.1	86.2	0.35
		537	136	210	105	69.4	107.2	64.7	2.4	116.7	0.23
		839	147	230	110	73.7	115.6	63.7	6.7	174.1	0.25
100 mm	33.2	201	124	180	25	50.6	73.7	68.6	0.9	242.8	0.80
		358	137	195	25	57.4	81.7	70.2	2.1	431.7	0.82
		559	169	230	25	73.8	100.7	73.3	5.9	674.5	0.85
	38.5	201	67	135	30	23.3	46.7	50.0	0.8	174.3	0.56

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		358	73	150	30	24.6	50.6	48.6	1.8	309.9	0.59
		559	76	180	30	22.5	52.9	42.4	5.1	484.3	0.61
	43.8	201	58	105	30	25.6	46.0	55.6	0.7	153.2	0.49
		358	64	120	30	27.1	50.7	53.5	1.6	272.3	0.53
		559	94	150	40	46.3	74.0	62.6	4.5	319.1	0.57
50 mm	33.2	101	52	60	15	26.6	30.9	86.2	0.5	202.3	0.71
		179	67	75	10	35.6	39.9	89.1	1.1	539.6	0.85
		280	81	90	10	43.3	48.2	89.8	3.0	843.1	0.88
	38.5	101	56	60	10	36.6	39.0	93.8	0.4	261.5	0.82
		179	68	75	10	42.4	47.0	90.3	0.9	464.9	0.85
		280	90	105	15	53.7	62.5	85.9	2.5	484.3	0.83
	43.8	101	31	30	10	25.4	24.5	103.7	0.4	229.7	0.68
		179	44	45	10	33.5	34.5	97.1	0.8	408.4	0.77
		280	58	60	10	44.3	45.8	96.8	2.2	638.2	0.83

As the flow of wastewater is increased from 33.2 mL/min to 43.8 mL/min, the breakthrough time decreased from 110 to 80 min (Table 3). The total time required for the adsorption is analogous to the stoichiometric capacity of the column and is found to be decreased from 162 to 122 min when the inlet concentration and bed volume is constant. However, there is an marginal increase in the fraction of the unused bed length from 0.32 to 0.35. The total percentage removal of ammonia increased from 65 to 67.9 %, while the adsorbent exhaustion rate increases from 82.8 to 86.2 g L−1 with an increase in the flow of wastewater. The bed saturation and the breakthrough time are obtained earlier with an increase in the flow due to the relatively rapid rate of mass transfer. The decrease in the breakthrough time may be a result of faster saturation of slag as the more molecules of ammonia and other toxicant present in the wastewater are available to saturate the active sites. Similar observation is found for the observations for the column of diameter 100 mm and 50 mm.

The effect of the mass of the adsorbent on the breakthrough curve is studied for variable mass that is 101, 179, 201, 280, 302, 358, 559, 537, 839 g depending on the bed height and column diameter. The other parameters such as the flow rate are maintained constant at 33.2, 38.5 and 43.8 mg L−1.

With an increase in the mass of the adsorbent from 302 to 839 g with a flow of 33.2 mg L-1 the time acquired for breakthrough is increased from 110 to 125 min and the total time required corresponding to the stoichiometric capacity of the column increases from 162 to 172 min. The total percentage removal of the ammonia decreased from 65 to 59.3 %, however, the fraction of the unused bed length decreased from 0.32 to 0.27 and the adsorbent exhaustion rate increased from 82.8 to 202.3 g L−1, respectively, with an increase in the mass of the adsorbent from 302 to 839 g. The adsorbent exhaustion rate increase with an increase in mass of adsorbent which depicts that more the adsorbent better is the removal efficiency but increase in unused bed length suggests that slag is not fully utilised. Similar observation is found for other studies done with the same bed height but with different column diameter. In the removal of ammonia studies fraction of the unused bed length was higher at 50 mm bed height and 43.8 mL/min and 101 g. Fraction of the unused bed length was minimum for 150 mm bed height and 839 g of slag with a flow of the wastewater at 33.2 mL/min. This shows that fraction of the unused bed length is affected by the bed height and flow.

D. Adsorption of thiocyanate

The observation on breakthrough curve for phenol as well as ammonia is also found to be true for the breakthrough curve of adsorption of thiocyanate as shown in Figure 5. Less bed height is found to be ineffective towards column studies.

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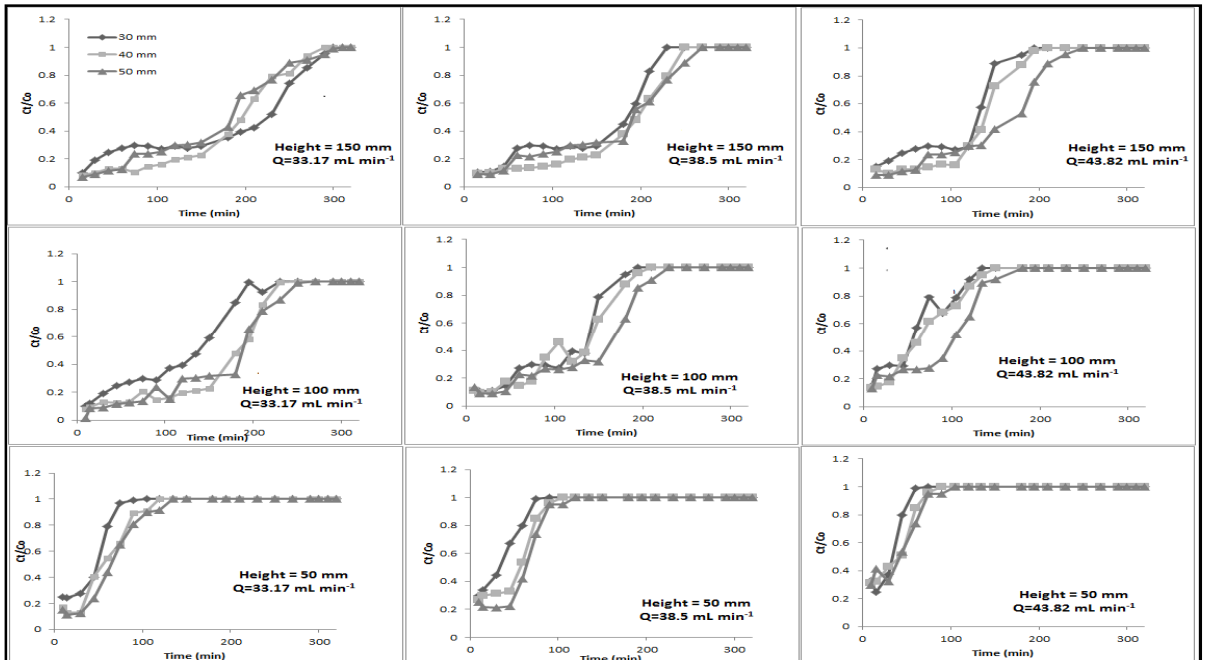


Figure 5: Breakthrough curves for thiocyanate adsorption

Table 4: Different parameters for the measurement of Thiocyanate adsorption in column studies

Column Height	Q (mL/min)	W(g)	t_t(min)	t_f(min)	t_b (min)	q_t(mg)	m_t (mg)	S %	EBRT	Ra (g/L)	Y
150 mm	33.2	302	193	290	150	136.9	205.3	66.7	1.4	60.7	0.22
		537	171	270	135	115.1	181.7	63.4	3.2	119.9	0.21
		839	221	300	105	172.1	234.1	73.5	8.9	240.9	0.52
	38.5	302	127	210	105	94.6	156.5	60.5	1.2	74.7	0.17
		537	130	230	100	91.0	160.6	56.7	2.8	139.5	0.23
		839	159	250	105	124.1	195.5	63.5	7.6	207.5	0.34
	43.8	302	124	180	120	120.3	174.2	69.0	1.1	57.4	0.03
		537	116	195	105	96.9	162.8	59.5	2.4	116.7	0.10
		839	151	230	105	139.8	212.3	65.8	6.7	182.3	0.31
100 mm	33.2	201	154	210	35	120.0	163.6	73.4	0.9	173.4	0.77
		358	144	230	60	95.1	152.4	62.4	2.1	179.9	0.58
		559	164	250	75	114.6	174.4	65.7	5.9	224.8	0.54
	38.5	201	120	180	45	99.0	148.2	66.8	0.8	116.2	0.63
		358	131	195	30	108.9	161.7	67.3	1.8	309.9	0.77
		559	136	210	30	108.0	167.1	64.6	5.1	484.3	0.78
	43.8	201	95	120	10	106.2	133.7	79.4	0.7	459.5	0.90
		358	105	135	15	114.5	147.2	77.8	1.6	544.6	0.86
		559	116	150	10	125.9	162.7	77.4	4.5	1276.4	0.91
50 mm	33.2	101	76	90	15	68.5	80.9	84.7	0.5	202.3	0.80
		179	82	105	30	68.7	87.5	78.5	1.1	179.9	0.64
		280	93	120	30	76.9	99.0	77.7	3.0	281.0	0.68
	38.5	101	66	75	10	71.4	81.2	87.9	0.4	261.5	0.85
		179	73	90	10	72.2	89.5	80.7	0.9	464.9	0.86
		280	83	105	30	80.5	102.0	78.9	2.5	242.1	0.64
	43.8	101	52	60	10	64.3	73.5	87.4	0.4	229.7	0.81
		179	64	75	10	77.7	90.4	86.0	0.8	408.4	0.84
		280	78	90	10	95.0	109.5	86.8	2.2	638.2	0.87

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As the flow of wastewater is increased from 33.2 mL/min to 43.8 mL/min, the breakthrough time decreased from 150 to 120 min (Table 4). The total time required for the adsorption is analogous to the stoichiometric capacity of the column and is found to be decreased from 193 to 124 min when the inlet concentration and bed volume is constant. However, there is significant decrease in the fraction of the unused bed length from 0.22 to 0.03. The total percentage removal of thiocyanate decreased from 60.7 to 57.4 %, while the adsorbent exhaustion rate decreased from 60.7 to 57.4 g L−1 with an increase in the flow of wastewater. The bed saturation and the breakthrough time are obtained earlier with an increase in the flow due to the relatively rapid rate of mass transfer. The decrease in the breakthrough time may be a result of faster saturation of slag as the more molecules of thiocyanate and other toxicant present in the wastewater are available to saturate the active sites. Similar observation is found for the observations for the column of diameter 100 mm and 50 mm.

The effect of the mass of the adsorbent on the breakthrough curve is studied for variable mass that is 101, 179, 201, 280, 302, 358, 559, 537, 839 g depending on the bed height and column diameter. The other parameters such as the flow rate are maintained constant at 33.2, 38.5 and 43.8 mg L−1.With an increase in the mass of the adsorbent from 302 to 839 g with a flow of 33.2 mg L-1 the time acquired for breakthrough is decreased from 150 to 105 min and the total time required corresponding to the stoichiometric capacity of the column increases from 193 to 221 min. The total percentage removal of the thiocyanate increased from 66.7 to 73.5 %, however, the fraction of the unused bed length and the adsorbent exhaustion rate increased from 0.22 to 0.52 and from 60.7 to 240.9 g L−1, respectively, with an increase in the mass of the adsorbent from 302 to 839 g. The adsorbent exhaustion rate increases with an increase in mass of adsorbent which depicts that more the adsorbent better is the removal efficiency but increase in unused bed length suggests that slag is not fully utilised. Similar observation is found for other studies done with the same bed height but with different column diameter.

In the removal of thiocyanate studies, fraction of the unused bed length was higher at 100 mm bed height and 43.8 mL/min and 201 g. Fraction of the unused bed length was minimum for 150 mm bed height and 537 g of slag with a flow of the wastewater at 33.2 mL/min. This shows that fraction of the unused bed length is affected by the bed height and flow.

D. Kinetic studies

K_{Th}, q_o were calculated for Thomas model and K_{YN} and τ were calculated for Yoon Nelson model. The values obtained are placed in Table 5. R^2 for both models was found to be same for each type of experiment. It has been observed that, when the mass of adsorbent was less the correlation coefficient (R^2) was very good for the removal of ammonia and phenol. As the mass of the adsorbent is increased the correlation coefficient started decreasing. The R^2 value decreased from 0.92 to 0.77 in cases of removal of ammonia and R^2 value decreased from 0.96 to 0.87. This shows that Thomas and Yoon Nelson Model fits well when the mass of the adsorbent in less. However, in case of removal of thiocyanate, correlation coefficient improves if the mass of adsorbent is high. The study reveals, phenol adsorbed per gram of the steel slagis 0.44 to 1.23 mg/g, ammonia adsorbed per gram of steel slag is 0.85 to 1.96 mg/g and thiocyanate adsorbed per gram of the steel slag is 0.07 to 0.32 mg/g of steel slag.

Table 5: Kinetic Model

Pollutant	Column Height	m (g)	q_o(mg/min)	Thomas		Yoon Nelson		R^2
				$K_{Th}*10^3$	q_o	K_{YN}	τ	
Thiocyanate	30	302	33	2.367	0.32	0.006	142.800	0.8426
	40	537	33	4.395	0.10	0.0101	95.347	0.9426
	50	839	33	3.842	0.07	0.0096	99.042	0.9631
Ammonia	30	302	33	0.384	1.96	0.0165	55.994	0.9239
	40	537	33	0.377	1.12	0.0162	54.889	0.8892
	50	839	33	0.319	0.85	0.0137	56.445	0.7733
Phenol	30	302	33	0.609	1.23	0.0262	36.874	0.9661
	40	537	33	0.551	0.69	0.0237	40.928	0.97
	50	839	33	0.591	0.44	0.0254	34.610	0.8791

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V. CONCLUSION

In the present work, steel slag is utilized as adsorbent for the removal of phenol, ammonia and thiocyanatein a fixed-bed column studies. The effect of the mass of adsorbent and flow rate is evaluated. In the study it has been observed that that fraction of the unused bed length is affected by the bed height and flow. Fraction of the unused bed length was minimum for 150 mm bed height and 537 g of slag with a flow of the wastewater at 33.2 mL/min for phenol and thiocyanate removal. Fraction of the unused bed length was minimum for 150 mm bed height and 839 g of slag with a flow of the wastewater at 33.2 mL/min for the removal of ammonia. It has been observed that, in case of removal of ammonia and phenol, Thomas and Yoon Nelson model fits well when the mass of adsorbent was less.The correlation coefficient (R^2) was very good. However, in case of removal of thiocyanate, Thomas and Yoon Nelson model fits well if the mass of adsorbent is high.

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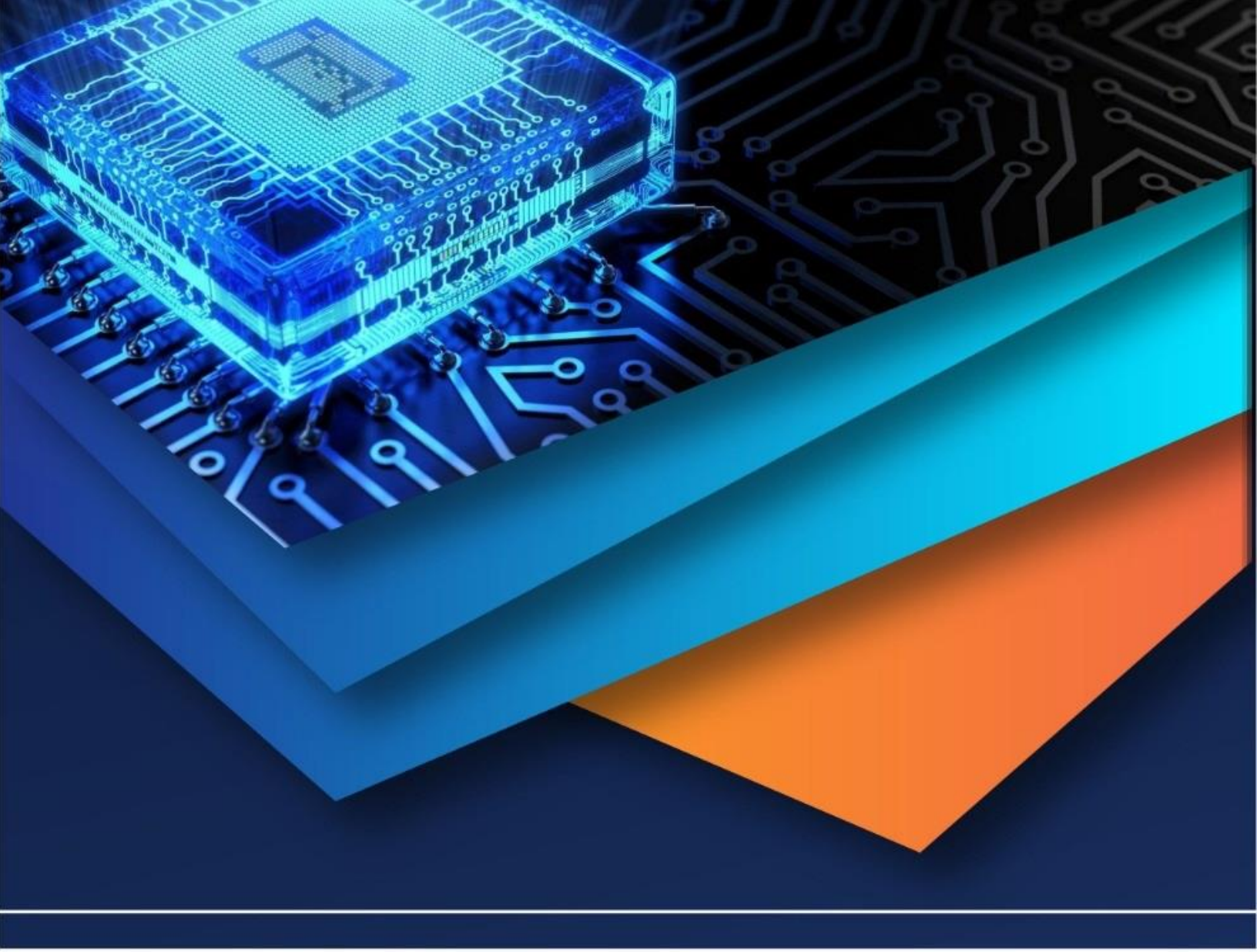
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