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Adsorption Potential of BF Slag and BF Flue Dust Towards Removal of Aqueous Phenol

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Abstract: ***The present work focus the removal of phenol present in industrial waste water (Steel Industry) using granulated BF slag and BF flue dust (generated as waste material in the steel industry). Several kinds of solid waste like granulated BF slag and BF flue dust and liquid toxic effluents are generated at different unit's process of integrated iron and steel plants. The study will help us to assess self-adsorption characteristics in plant generated solid water Vs in plant toxic effluents. In the study shows that granulated BF slag and BF flue dust are efficient adsorbents for the removal of phenol from the industrial waste water.***

Keywords: Adsorption, BF Flue Dust, Equilibrium Isotherms, Equilibrium Kinetics, Granulated BF Slag, Phenol, Sorption, Wastewater.

INTRODUCTION

The steel industry produces waste materials as much as or even more than any other manufacturing industries [1].
Million tons of steel are produced per year and this in return, produces million tons of wastes in the form of slag, dust, sludge, effluents and other pollutants. Some the wastes generated are recycled in the process of sintering and water harvesting, but certain pollutants are very much threat to biological organisms. Many industrial wastes contain organics and which are difficult or impossible to remove by the conventional biological treatment process.

Phenol is the priority pollutant since it is toxic and harmful to organisms even at low concentration. Besides the toxic effects, phenolic compounds create an oxygen demand in receiving waters and impart taste and odour to water with minute concentrations of their chlorinated compounds. Surface and ground waters are contaminated by phenolic as a result of the continuous release of these compounds from petrochemical, coal conversion and phenol producing industries. Therefore, the wastewaters containing phenolic compounds must be treated before their discharging into the water streams [2, 3, 4].

Adsorption of phenol from an aqueous solution of activated carbon with different oxygen content was conducted by S. Binaik, J. Kazmierczak and A. Swiatkowski, Adsorption Sci. Technol., 6 (4), 182-191, (1989)
Conventional methods for the removal of phenolic pollutants in aqueous solutions can be divided into three main categories: physical, chemical and biological treatment [5]. Among them, physical adsorption method is generally considered to be the best, effective, low cost and most frequently used method for the removal of phenolic pollutions. Therefore, the search for low cost and easily available adsorbents has led many researchers to search more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Recently, using the inorganic materials as adsorbents has become one hot research field [6].

Adsorption as a simple and relatively economical method is a widely used technique for the removal of pollutants.

Although the adsorbent used may vary due to the change in adsorption condition depending on the type of pollutants.

MATERIAL & METHODS

Adsorbents Granulated Blast furnace slag & Blast furnace Flue Dust collected from NINL stack yard.

Materials used for Phenol adsorption:

(i) Granulated BF slag (GBFS).
(ii) BF Flue Dust (BFFD)
(iii) H_2SO_4 (1:1)
(iv) D.M. Water, (v) Phenol (AR grade)

Table: 1 Chemical Composition

Parameters (%)	GBFS
SiO_2	31.00 %
Al_2O_3	23.21 %
CaO	32.64 %
MgO	10.33 %
FeO	0.32 %
MnO	0.33 %
S	0.76 %
Basicity (CaO/SiO2)	1.05

Table: 2 Chemical Compositions

Parameter (%)	BFFD
T. Fe (%)	33.201
SiO_2 (%)	6.389
Al_2O_3 (%)	5.520
CaO (%)	7.965
MgO (%)	1.658
C (%)	29.666
LOI (%)	30.666

Apparatus Used:

(i) Distillation apparatus
(ii) Spectrometer

Reagent for Phenol:

(1) **Phosphate Buffer**
For 1 ltr.
Dissolve 104.5 gm K_2HPO_4 and 73.3 gm K_2HPO_4 in H_2O and dilute to 1 ltr.

(2) **4-Amino Antipyrine solution:**
Dissolve 2 gm. 4-amino antipyrine in water and dilute to 100 ml.

(3) **Potassium Ferricyande:**
Dissolve 8 gm $K_3Fe(CN)_6$ in H_2O and dilute to 100 ml.

(4) **NH_4OH = 0.5 N**
9.5 ml of NH_3 in 250 ml of D.M. water
K_2HPO_4 - di-patassium hydrogen phosphate.
K_2HPO_4 - Potassium dihydrogen phosphate.

Calculation:

Then the two samples are placed is Spectrophotometer.
The reading of the spectrophotometer gives the absorbance of the sample.
Measure Absorbance at 510 mm.

$$\text{Phenol PPM} = \frac{\text{Absorbance x factor x 1000}}{\text{Sample Volume}} \text{ X Dilution factor}$$

Determination of phenol by chloroform extraction method:

Procedure: 100 ml of sample was taken in a 250 ml beaker and 30 to 50 ml of DM water was added to it. PH of the sample was adjusted to 4.0 by adding phosphoric acid (dilute) and NH_4OH(dilute). Then the sample was transferred to a distillation flask and distillation was done. 100 ml of distillate was collected and was transferred to a 250 ml beaker and the following chemicals were added [7].

1. 2.4 ml 0.5N NH_4OH solution
2. 2 ml phosphate buffer
3. pH was adjusted to 7.9 by phosphate buffer or dilute NH_4OH or acetic acid.
4. 0.6 ml of aminoantipyrine solution (2%)
5. 0.6 ml $K_2Fe(CN)_6$ solution (8%)

This solution was transferred to a 250 ml separating funnel, shacked well and stand for 10 minutes for colour development. 10 ml of chloroform was added and shacked for 5 minutes. The chloroform extract was filtered through 41 filter paper containing 2 gm of anhydrous sodium sulphate, directly into a dried cell or cuvette and the absorbance was measured at 460 nm photo spectrometer. A blank sample was prepared in the same manner with DM water.

Calculation:

Phenol in PPM = Absorbance x 0.58.

Table3: Adsorption of Phenol (20 ppm) on BF Slag (0.500 gm)

Time (min)	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e=(C_o-C_e)V/m}
5	0.084	3.150	16.850	33.700
10	0.076	2.850	17.150	34.300
20	0.068	2.550	17.450	34.900
30	0.050	1.875	18.125	36.250
40	0.050	1.875	18.125	36.250

Table4: Adsorption of Phenol (50 ppm) on BF Slag (0.500 gm)

Time min	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e=(C_o-C_e)V/m}
5	0.133	4.987	45.013	90.026
10	0.083	3.12	46.88	93.76
20	0.053	2.00	48.00	96.00
30	0.026	1.00	49.00	98.00
40	0.026	1.00	49.00	98.00

Table 5: Adsorption of Phenol (100 ppm) on BF Slag (0.500 gm)

Time min	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e= (C_o-C_e)V/m}
5	0.400	15.000	85.000	170.000
10	0.338	12.675	87.325	174.650
20	0.297	11.137	88.863	177.726
30	0.267	10.012	89.988	179.976
40	0.267	10.012	89.988	179.976

Table6: Adsorption of Phenol (20 ppm) on BF Flue Dust (0.500 gm)

Time min	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e= (C_o-C_e)V/m}
10	0.052	1.950	18.050	36.100
20	0.050	1.875	18.125	36.250
30	0.048	1.800	18.200	36.400
40	0.029	1.080	18.920	37.840
50	0.025	0.937	19.063	38.126
60	0.025	0.937	19.063	38.126

Table7: Adsorption of Phenol (50 ppm) on BF Flue Dust (0.500 gm)

Time min	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e=(C_o-C_e)V/m}
10	0.285	10.687	39.313	78.626
20	0.280	10.500	39.500	79.000
30	0.275	10.312	39.688	79.376
40	0.268	10.050	39.950	79.900
50	0.265	9.937	40.063	80.126
60	0.265	9.937	40.063	80.126

Table8: Adsorption of Phenol (100 ppm) on BF Flue Dust (0.500 gm)

Time min	Absorbance	Phenol remain in ppm (C_e)	Phenol Adsorbed in ppm (C_o-C_e)	Phenol Adsorbed in mg/gm {q_e=(C_o-C_e)V/m}
10	0.489	18.337	81.663	163.326
20	0.485	18.187	81.813	163.626
30	0.450	16.875	83.125	166.250
40	0.443	16.612	83.388	166.776
50	0.435	16.312	83.688	167.376
60	0.435	16.312	83.688	167.376

Kinetic Study

Effect of Contact Time and Initial Concentration of Phenol

The contact time experiment of adsorption of phenol on granulated BF slag and BF flue dust is carried out by agitating fixed amount of phenol with 0.5 gm of the adsorbent for various time intervals. From this study it is found that amount of phenol adsorbed, increases with increase in time and after 150 min for 30 min for granulated BF slag and 50 min for BF flue dust, it remains more or less constant. Hence for further kinetic study and equilibrium time of 150 min was selected for 30 min for granulated BF slag and 50 min for BF flue dust.

The effect of initial concentration of phenol on adsorption is studied at three different concentrations i.e. 20 ppm. 50 ppm and 100 ppm. The effect of initial concentration of phenol on adsorption on BF slag and Bf flue dust is shown in fig 3 to 8.

It is seen that adsorption of phenol on granulated BF slag and BF flue dust is found to be concentration dependent. The removal of phenol increases with increase in initial concentration whereas the percentage removal decreases. This is in agreement with the finding, that the rate of uptake of adsorbate is found to increase non-linearly with increasing concentration of solute. The values of various pseudo-second order rate constant are listed below.

Table 9: Pseudo- second order kinetic constants for Adsorption of phenol on granulated BF slag and BF flue dust

Adsorbent	Concentration mg/ltr	K (g/mg.min)	q_e (mg/gm)	h (mg/gm.min)	r (regression constant)
BF Granulated Slag	20	0.0009	36.25	1.2	0.9991
	50	0.00035	94.9	3.16	0.9996
	100	0.00018	179.97	5.99	0.9998
BF Flue Dust	20	0.0005	38.126	0.76	0.9995
	50	0.00024	80.126	1.60	0.9997
	100	0.00019	167.376	3.35	0.9998

From the above table, it is observed that The experimental data obtained with varying concentrations of phenol follows pseudo-second order equation with regression constant greater than 0.99. The initial adsorption capacity of phenol on granulated slag and BF flue dust increases with increase in initial concentration.

Table10: Intra-particle diffusion rate constants for adsorption of phenol on granulated slag and BF flue dust at different initial concentration

Adsorbent	Initial Concentration (mg/l)	$K_p = q_e/t^{0.5}$ (mg/g.min$^{0.5}$)
BF Granulated Slag	20	6.618
	50	17.326
	100	32.85
BF Flue Dust	20	5.391
	50	11.331
	100	23.670

The above table shows the infra-particle diffusion calculation by using the equation

$q = K_p x t^{0.5}$

Isotherm Studies

Adsorption isotherms of phenol on granulated BF slag and BF flue dust were obtained by stirring the various concentration of phenol (20, 50, 100 ppm) with 0.500 grams of adsorbent. The adsorption isotherms thus obtained as shown in the fig. 1 to 4 from the nature of the curve this isotherm can be classified as L type according to the Gile's classification system. It can be seen that the amount of phenol adsorbed increases in increasing in concentration and time after particular concentration and time it remains more or less constant of phenol on granulated slag is shown in the figure. It is seen from the linearity of plots in fig. 5 & 6 that adsorption phenol on granulated slag follows both isotherms models with regression constant greater than 0.9. The value of Freundlich and Langmuir constants are listed in table 11.

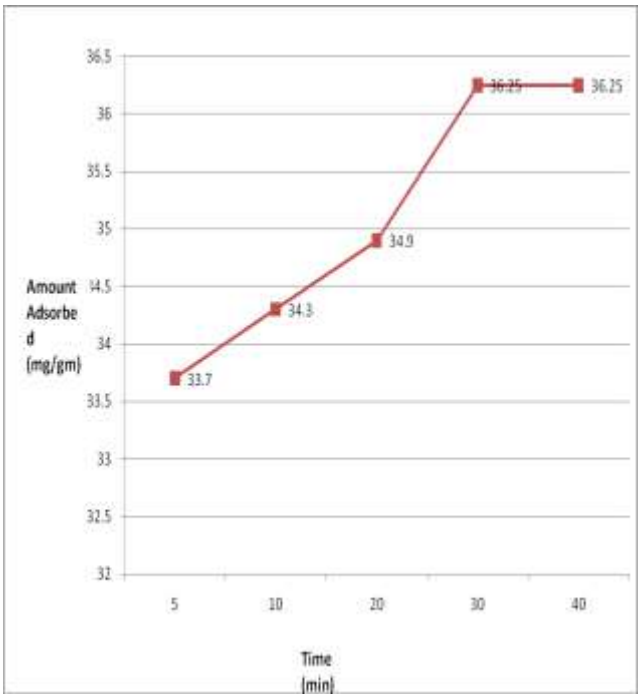

Fig: 1 Adsorption of Phenol 20 ppm on BF slag

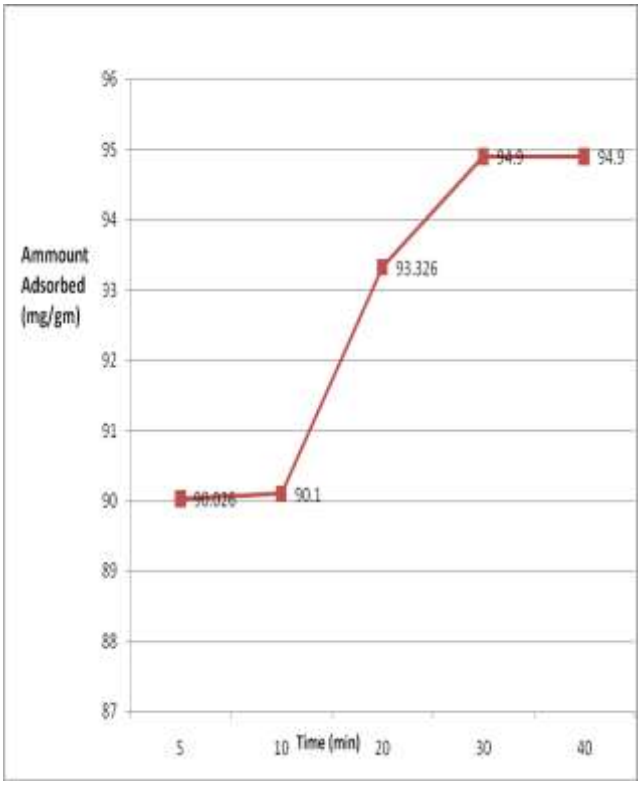

Fig: 2 Adsorption of phenol, 50 ppm on BF slag

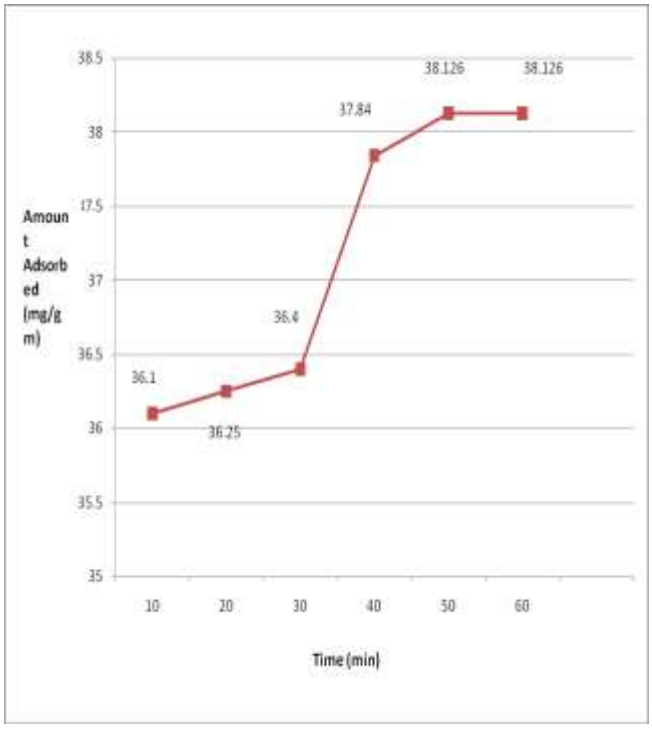

Fig: 3 Adsorption of phenol, 20 ppm on Flue dust

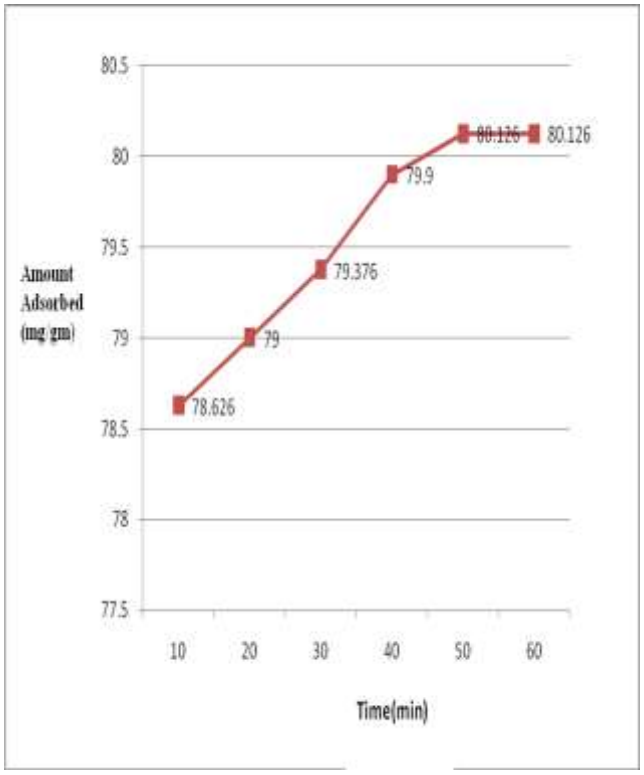

Fig: 4 Adsorption of phenol 50 ppm on BF flue Dust

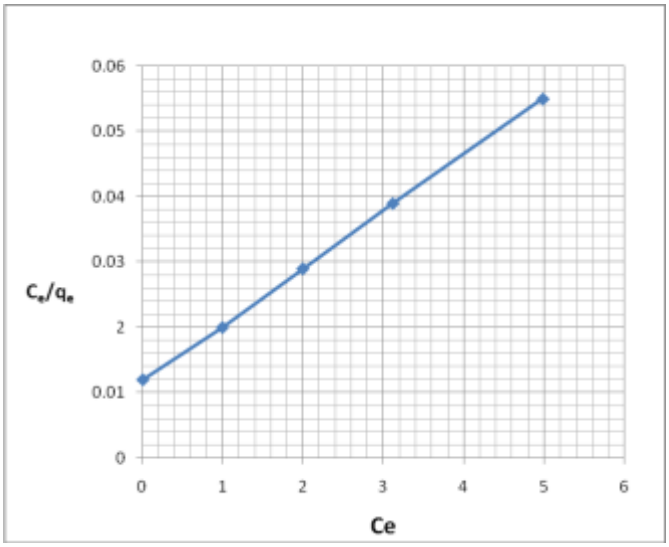

Fig 5 Langmuir Isotherm for phenol (50 ppm) adsorption on BF Granulated Slag

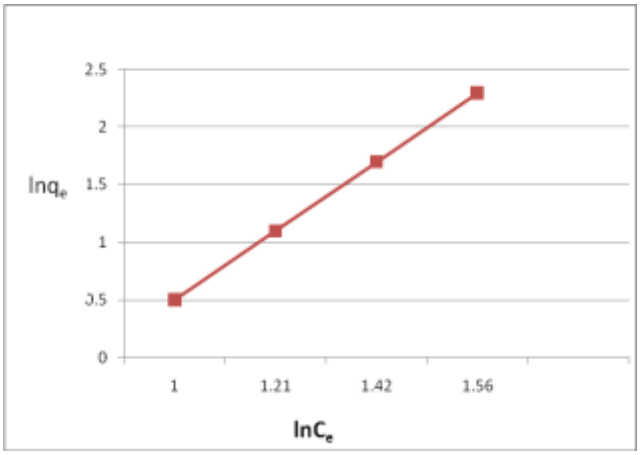

Fig 6 Freundlich Isotherm for Phenol (50 ppm) adsorption on BF Granulated Slag

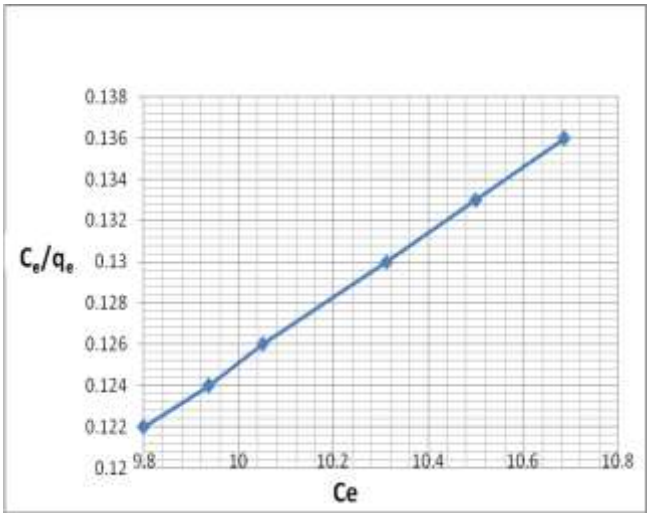

Fig 7 Langmuir Isotherm for phenol (50 ppm) adsorption on BF Flue Dust

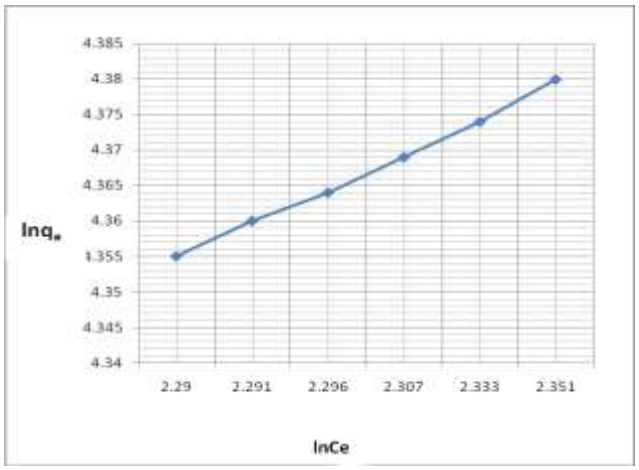

Fig 8: Freundlich Isotherm for Phenol (50 ppm) adsorption on BF Flue Dust

Table 11: Parameter of and Freundlich Isotherm Models for Adsorption of Phenol (50 ppm) on Granulated BF Slag

Langmuir Constant			Freundlich Constant		
q_0 (mg/g)	K_L	R^2	K_f	1/n	R^2
98	0.02	0.9985	0.2	1.602	0.9928

From the above table, it can be seen that the value of co-relation factor R^2 is close to the unit for both models which indicate the good representation of the experimental results by using linear Langmuir or Freundlich isotherm.

The influence of various factors such as initial concentration, amount of adsorbent, pH, and bed height on adsorption capacity has been studied. The percentage removal of phenol is observed to increase with the increase in contact time and after sometimes it attains the equilibrium for BF slag and flue dust it is 150 min, 30 min, 50 min. respectively. The experimental data were analysed by Langmuir and Feudlich models in order to describe the equilibrium isotherm. Equilibrium data fitted well to the Langmuir model correlating constant R^2 higher than 0.998. The kinetic of adsorption of phenol studied, it is observed that the experimental data obtained with varying concentrations regression constant great than 0.99.

CONCLUSION

It is inferred from the above observation that granulated BF slag and BF flue dust shows good adsorption capacity to remove phenol from wastewater. The result indicated that the percentage removal of phenol was considerably affected by initial phenol concentration, amount of adsorbent dose and mixing contact time. The result showed that the percentage of removal increased with increasing the adsorbent dosage. The result also indicates that uptake of phenol took place at natural pH value and equilibrium happens at 30 minutes for BF granulated slag and 50 minutes for BF flue dust. The kinetics of adsorption of phenol granulated BF slag and BF flue dust can be explained satisfactorily using pseudo-second order model with regression coefficient greater than 0.99. The Langmuir and Freundlich adsorption model was used for the mathematical description of adsorption model. The obtained results show that the adsorption equilibrium data fit very well to both models.

Hence, BF granulated slag, BF flue dust can be used as an effective and alternative adsorbent for sorption of phenol from industrial wastewater, thus reduce pollution.

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