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Adsorption of nickel ions from leachate on groundnut shell activated carbon

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Abstract

It has been widely recognized that heavy metal removal by activated carbon adsorption is due to the surface complex formation between the metal ions and the acidic surface functional groups. The present study focuses to investigate the possibility of the utilization of activated carbon prepared from groundnut shell as a low cost adsorbent material for the adsorption of heavy metal present in the leachate. Batch experiments were conducted to determine the effect of contact time, pH, adsorbent dosage, speed of agitation, temperature. Experimental data was evaluated to find out kinetic characteristics of the adsorption process. The isothermal data was well described by the Freundlich and D-R adsorption model with a fit ($R^2 = 0.964$). The maximum % removal of Nickel ions was observed to be 95% at pH =10 with speed of agitation = 500 rpm and 25ºC temperature.

Keywords: activated carbon, groundnut shell, GSAC (groundnut shell activated carbon), leachate treatment

1. Introduction

Pollution load of the environment is increasing due to global rise in population and our quest to lead comfortable life resulting in explosive growth of industrial and agricultural activities. Environmental contamination with metal ions represents a potential threat to human, animals and plants. Metal ions which many of them are soluble in aqueous solution become more available for living system and accumulate in the environment are of vital concern.

Nickel is released into the environment in a large number of processes such as electroplating and steel manufacturing. In general, to be removed from wastewater, the metal must be precipitated or otherwise attached to an insoluble form through ion-exchange or adsorption [1]. For the present study groundnut shell activated carbon (GSAC) is used for adsorption method for removing Nickel metal from leachate.

2. Materials and Methods

2.1 Preparation of adsorbent

Activated carbon from groundnut shell was prepared by treating it with potassium hydroxide. Initially the material was washed thoroughly with water to remove earthy matter and dried at 110 ºC. The dried material was then subjected to 1 N KOH 150ml for 10 min. This material was then washed with dilute HCl to make sample neutral. It was then carbonized at 500 ºC for 25 min in muffle furnace. Finally the material was ground in an agate mortar and then sieved to 16 mesh size. Various optimization conditions during lower and higher carbonization conditions were obtained for the preparation of adsorbent based on percentage yield and adsorption efficiency [2-17].

2.2 Properties of adsorbent

Physical characteristics of GSAC were estimated in terms of particle size, apparent density, surface area and surface functional groups. [See Table 1 and Table 2].

Table 1: Proximate analysis

S. No.	Parameter	Values
1	Moisture	9
2	Ash	8.2
3	Volatile matter	11.4
4	Fixed carbon	71.4

Table 2: Physical and adsorptive characteristics of activated carbon

S. No.	Parameter	Values
1	Apparent density(g/cm^3)	0.23
2	Iodine value	1114
3	Methylene number	238
4	Surface area(m^2/g)	364.023

Moisture, ash and volatile matter was determined by heating 1gm of GSAC at 100 ºC, 800 ºC and 900 ºC respectively to constant weight. The difference in weight was calculated and expressed in percentage [18].

2.3 Batch Adsorption Experiment

The batch sorption studies were carried out by shaking series of bottle containing different amount of adsorbent and leachate sample. The leachate sample containing different dosages of activated carbon were shaken for six hours to determine the effect of speed of agitation, loading, temperature and pH. Both SEM and FTIR analysis were carried out on activated carbon prepared from groundnut shell to find out modification in the morphology and functional group. In order to obtain adsorption capacity, the amount of ions adsorbed per mass of carbon was evaluated using following expression.

$$Q_e = (C_o - C_e)\frac{V}{M} \quad (1)$$

Where C_o and C_e are concentration of Nickel before and after interaction with the activated carbon, Q_e is the adsorption capacity (mg/g), V is volume of the leachate sample taken and M is the weight of activated carbon (g) [19].

2.4 Characteristics of adsorbent

2.4.1 Fourier Transform Infrared Spectroscopy

Figure 1 represents FTIR spectra of GSAC. The peaks at 2916 and 1393 per cm in the spectra are due to stretching and bending vibration of C-H respectively. A band at 1100 per cm is observed due to Co stretch vibration in acids, alcohols, phenols, ethers and/or esters.

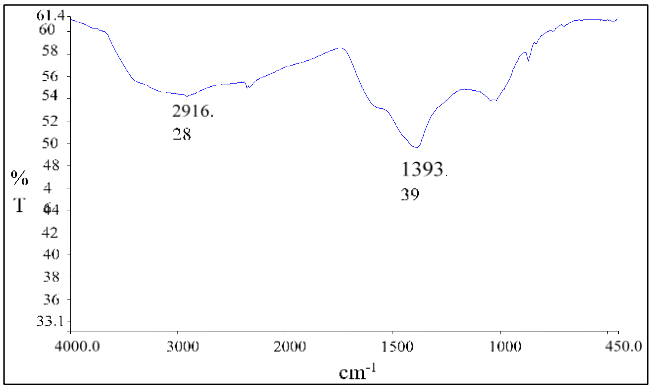

Fig 1: FTIR spectra of GSAC

2.4.2 X- ray diffraction measurements

X-ray diffraction pattern of sample were obtained using advanced diffractometer (for 2θ range from 10° to 80°) with monochromatic CuK alpha radiation to identify crystalline nature of sample.

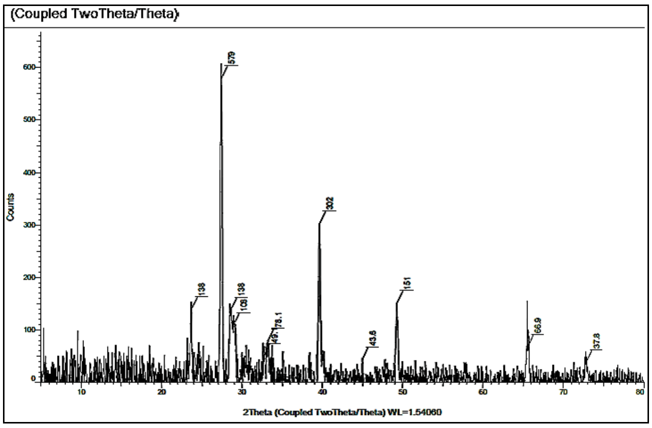

Fig 2: X- Ray diffraction [XRD] image of GSAC

2.4.3 Scanning Electron Microscopy and Energy dispersive X-ray Spectroscopy

Scanning Electron Microscopy [SEM] micrographs (Figure 3) of activated carbon prepared from groundnut shell were obtained. It is observed that the larger particle sizes of grains have elongated spherical morphology. Boundaries of grains are clearly seen in the SEM micrograph.

Energy dispersive X-ray spectrometry analysis of GSAC (Figure 4) shows peaks for potassium, manganese and gold element. There is no trace of any other impurities seen within the detection limit of the EDX as presented in the figure.

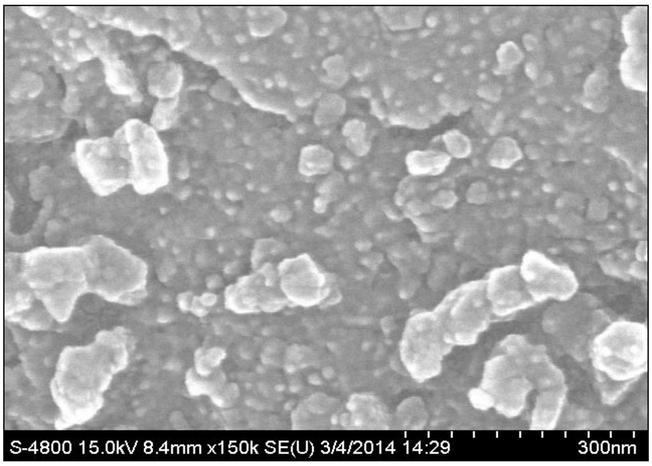

Fig 3: Scanning Electron Microscopy [SEM] image of GSAC

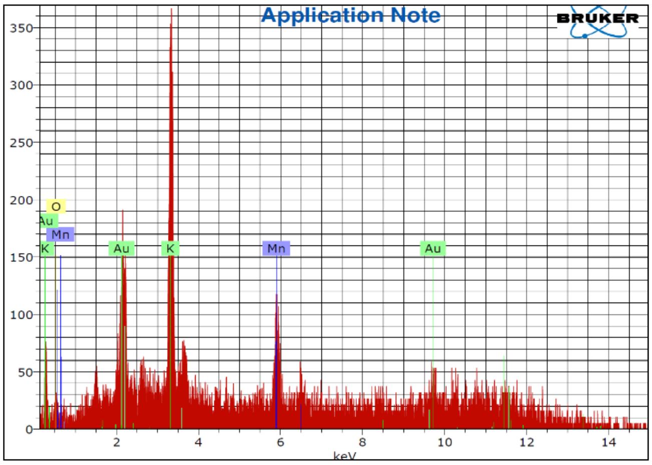

Fig 4: Energy dispersive X-ray Spectroscopy [EDX] of GSAC

2.4.4 Nitrogen (N_2)-BET

BET was carried out using Micromeritics Chemisorb 2720 instrument for 16 mesh GSAC. The surface area were found to be 364.023 m^2/gm [20]. If surface area is so low then adsorption is due to what we have to justify.

3. Results & Discussion

3.1 Effect of parameter

The GSAC prepared with the method described in section 2.1 above was used to adsorb the heavy metal ions. The studies were carried out by varying the parameters like leachate volume, pH, speed of agitation, temperature and loading.

3.1.1 Effect of Leachate volume

To investigate the effect of leachate volume dose on adsorption of GSAC in leachate, the experiment were conducted with varying leachate volume from 25 ml to 100 ml and it was found that with an increase in leachate volume % removal decreases. At higher leachate volume the concentration of Ni in sample is high as compared to availability of the adsorption sites. The % removal was not found proportional to adsorbent dosage. It was just notified that with increase in leachate volume the increase in % removal is not proportionally high.

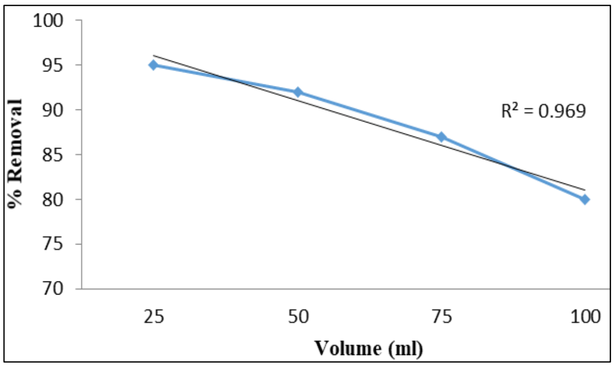

Fig 5: Effect of leachate volume (Temperature 25 ºC, Pressure 1 atm)

3.1.2 Effect of pH:

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ion concentration and the degree of ionization of the adsorbate during reaction. To investigate the effect of pH on adsorption of GSAC in leachate, the experiments were conducted with varying pH. The percentage of metal ion removed increases as pH increases and maximum at pH = 10. At low pH, the surface adsorption sites are closely linked to the H^+ ions, thereby making these unavailable for other cations.

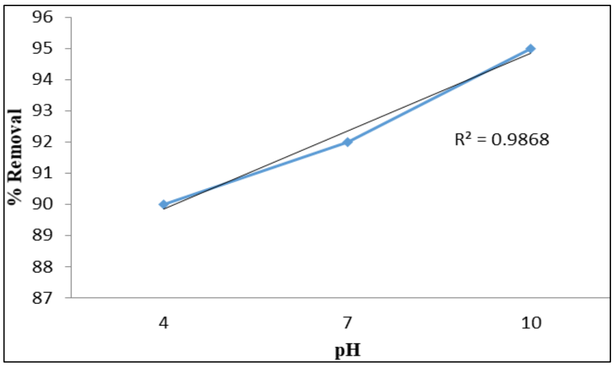

Fig 6: Effect of pH (Temperature 25 ºC, Pressure 1 atm)

3.1.3 Effect of speed of agitation

To determine the effect of speed of agitation, runs were conducted with 500, 800 and 1200 rpm with 6 gm of GSAC and 100 ml of leachate sample. The study shows that with increasing speed of agitation adsorption increases (Figure 7). Maximum adsorption observed at 500 rpm. Any further increase or decrease in speed of agitation did not cause significant change in adsorption. This indicates that agitation rate 500 rpm was sufficient to assure that all the surface binding sites are readily available for metal uptake.

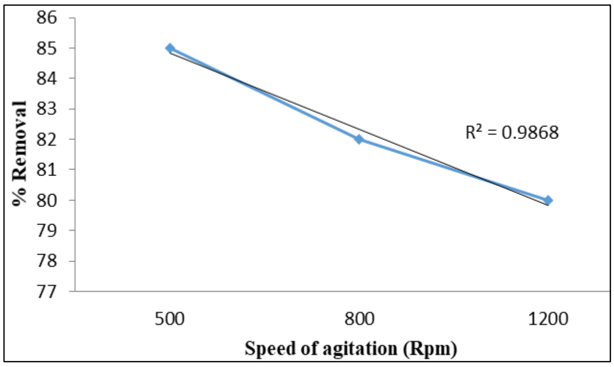

Fig 7: Effect of speed of agitation (Temperature 25 ºC, Pressure 1 atm)

3.1.4 Effect of temperature

The effect of temperature on adsorption for Ni was studied at 25 ºC, 35 ºC and 50 ºC. The results are presented in figure 8. The maximum adsorption of Nickel ion was obtained at 25 ºC. As the temperature increases the kinetic energy of metal ions in solution also increases to make the number of metal ions reaching to the adsorbent surface maximum. The observed decrease in percentage removal with increase in temperature suggests weak binding interaction between the active sites and the metal hence the extent of adsorption generally increases with decrease in temperature.

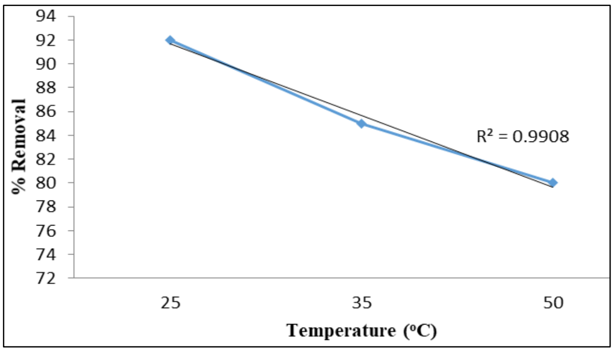

Fig 8: Effect of temperature, Pressure 1 atm)

3.1.5 Effect of loading

The effect of adsorbent dosage on adsorption of nickel was studied in the range of 0.25 to 3 gm (Figure 9). The increase in the adsorption percentage with rise in adsorbent dosage may be due to increase in the available adsorption active sites on the adsorbents and thus making easier penetration of the metal ion to the sorption sites. However, any further addition of the adsorbent beyond the obtained optimum masses did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles and also due to decrease in the contact time required to reach apparent equilibrium as the adsorbent dose increases.

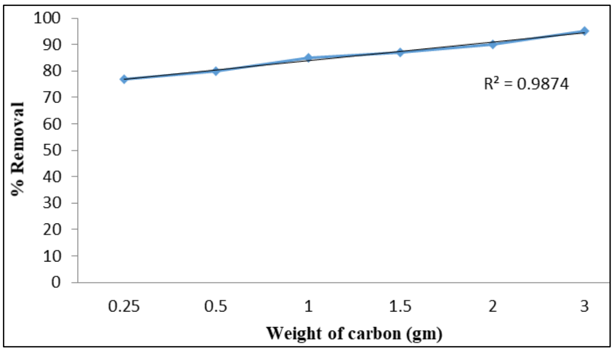

Fig 9: Effect of loading (Temperature 25 ºC, Pressure 1 atm)

3.2 Study of Isotherm

The adsorption isotherm data are important to study the adsorption capacity and equilibrium coefficient for adsorption process. In the present work, three adsorption isotherms were utilized viz. Freundlich, Langmuir and D-R isotherm. In this study, adsorption isotherm models were evaluated using three parameters such as temperature variation, contact time variation and also using adsorbate concentration variation [21].

3.2.1 Langmuir Isotherm

The Langmuir isotherm is applied to homogeneous sorption.

It is the simplest theoretical model for monolayer adsorption which was developed from kinetic or thermodynamic derivation. The equation for Langmuir isotherm is given below,

$$\frac{C_e}{q_e} = \left(\frac{C_e}{Q}\right) + \left(\frac{1}{bQ}\right) \qquad (2)$$

"Q" and "b" in this case can be determined from the plot of C_e/q versus C_e (Figure 10). "Q" indicates the maximum sorption upon complete monolayer saturation. Higher value of "b" indicates the adsorbent has high affinity for the adsorbate and vice versa.

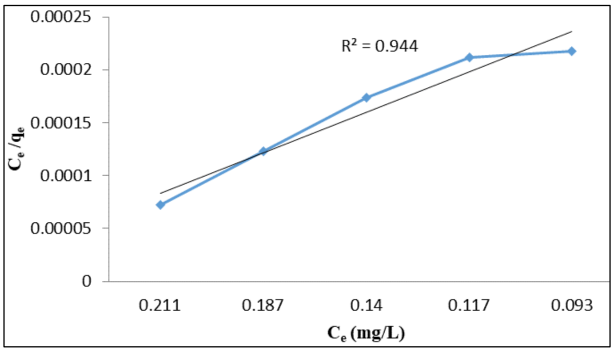

Fig 10: Langmuir isotherm

3.2.2 Freundlich Isotherm

It is an empirical isotherm model that considers heterogeneous adsorption and can be used for non-ideal adsorption. The equation for Freundlich isotherm is given below,

$$q_e = K_f * C_e^{1/n} \qquad (3)$$

The results revealed that the adsorption of nickel under optimum condition at 25 °C obeyed Freundlich isotherm (Figure 11). This model represents the relationship between the amount of Nickel adsorbed per unit mass of the adsorbent (q_e) and concentration of Nickel (C_e). K_f and n are constant representing the adsorption capacity and intensity of adsorption. Higher value of n indicates greater degree of heterogeneity. For 1/n less than unity, adsorption is the predominant process that takes place otherwise desorption becomes predominant [22].

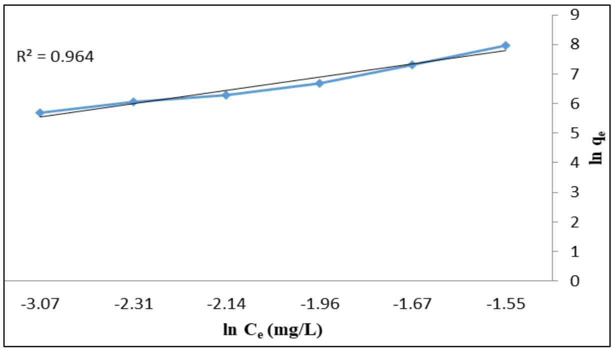

Fig 11: Freundlich isotherm

Figures11 and 12 show Langmuir and Freundlich isotherm graphs respectively which suggests that Freundlich isotherm gives best fit between experimental and theoretical data.

3.2.3 Dubinin-Radushkevich Isotherm

The D-R isotherm which assumes a heterogeneous surface is expressed as follows

$$lnq_e = lnq_m - K * e^2 \qquad (4)$$

The parameter e can be found from equation,

$$e = RTln\left[1 + \frac{1}{C_e}\right] \qquad (5)$$

Where K Constant related to adsorption energy, q_e is amount of Ni ions adsorbed per unit mass of adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), R is gas constant and T is absolute temperature.

Therefore D-R isotherm (Figure 12) can be used to predict equilibrium adsorption data at different temperatures. The model describes the adsorption of subcritical vapors onto micro pore solids following a pore filling mechanism. The plot of ln q_e vs e^2 gives slope K (mol^2/J^2) and intercept q_m. [23].

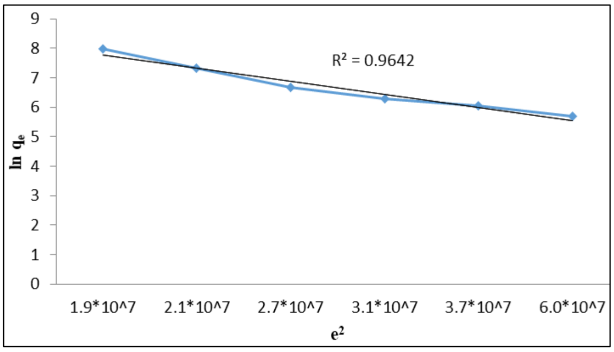

Fig 12: Dubinin-Radushkevich isotherm

The results of all the three isotherm studies are tabulated in Table 3.

Table 3: Isotherm parameters determined with varying adsorbent dosage

Isotherm model	Parameter	Values
Langmuir	R^2	0.944
Freundlich	K_f mg/g(L/mg)$^{1/n}$ 1/n R^2	3751 -0.445 0.964
D-R	R^2 E (KJ/mol)	0.964 7807

3.3 Kinetic studies

The adsorption kinetic studies describe the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solid-liquid interface. Adsorption kinetics is one of the important characteristics in defining efficiency of adsorption process and to understand the behavior of adsorbent [24].

3.3.1 Pseudo-First-Order Model

$$log(q_e - q) = logq_e - K_f \frac{t}{2.303} \qquad (6)$$

$$q = (C_o - C_e) * \frac{V}{M} \qquad (7)$$

Where C_o and C_e are initial and equilibrium adsorbate concentration in solution, V is volume of solution, M is mass of adsorbent and K_f is a rate constant for pseudo-first-order model (1/min).

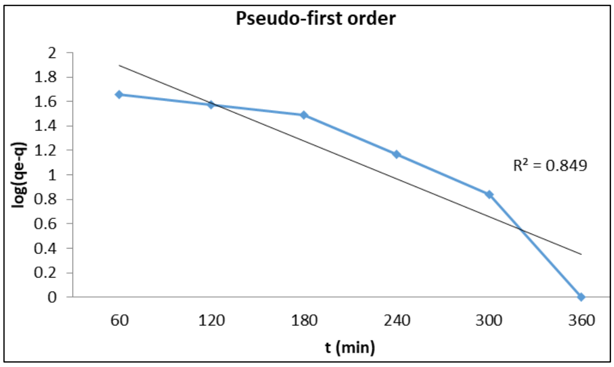

Fig 13: Pseudo-first order model

The figure 13 shows the result of pseudo-first order model when applied to the experimental data of adsorption.

3.3.2 Pseudo-Second-Order Model

Pseudo-second order equation is based on the assumption that rate limiting step may be chemical adsorption. It is assumed that adsorption capacity is proportional to the number of active sites occupied on the adsorbent. The equation of pseudo-second order is given below.

$$\frac{t}{q} = \frac{q}{K_s} * q_e^2 + \left(\frac{1}{q_e}\right) t \qquad (8)$$

Where, K_s is a rate constant for pseudo second order model (g/mg. min). The initial sorption rate, the equilibrium sorption capacity and pseudo-second order rate constant can be determined from plot t/q vs. t [Figure 14]. As a result, the sorption system appears to follow pseudo-second order kinetics [25].

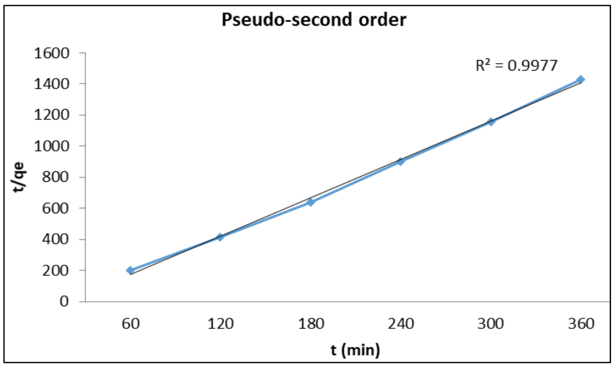

Fig 14: Pseudo-second order model

The pseudo-second order model for adsorption of metal ions onto GSAC agrees well with experimental data due to greater value of R^2 i.e., 0.997. These suggest that adsorption data is well represented by pseudo-second order kinetics and supports assumption that rate limiting step of metal adsorption may be chemical adsorption.

4. Conclusions

The present work shows that groundnut shell based powdered activated carbon; GSAC is an effective adsorbent for removal of Nickel ions from leachate. The percent removal was observed around 95% at pH 10. The Langmuir, Freundlich and D-R isotherm could be used to model isotherm sorption of heavy metal on GSAC but the Freundlich isotherm gives the best fit (R^2 = 0.964). The kinetic data follows pseudo-second order model. (R^2= 0.997)

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