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ADSORPTION CAPACITY OF RICE HUSK FOR SILVER IONS BY LANGMUIR ISOTHERM METHOD

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The adsorption of silver ions on rice husk has been studied in nitric acid medium at ambient temperature using batch method. Atomic absorption spectrometry was employed for the quantification of silver ions. Maximum adsorption was observed at nitric acid concentration of 0.001mol L^{-1} using 0.5 g of rice husk and shaking time of 15 minutes. The adsorption of silver ions obeyed the Langmuir isotherm model in the concentration range of 1.854×10^{-4} to 1.159×10^{-3} mol L^{-1}. A comparison of four linear equations of the Langmuir isotherm (Type 1, 2, 3 and 4) were examined for silver ion sorption onto rice husk. Isotherm parameters obtained from the four linear equations are reported and discussed. Though Langmuir type 1 is the most popular form, but the type 2 had the highest correlation coefficient of R^2 = 0.9967, compared with the other Langmuir linear equations with R^2 values ranged from 0.9688 to 0.9937. The observed adsorption capacities (Q_m) of the silver ions on rice husk were in the range of 1.08 to 1.62 mg g^{-1}. The determined adsorption capacity of silver on rice husk was also compared with the reported values for other adsorbents.

Keywords: Adsorption capacities, Rice husk, Silver ions, Langmuir isotherm

1. Introduction

Silver (Ag) is a white naturally occurring one of the precious metals and is stable in acidic medium. Silver and its compounds are being consumed in modern technology such as electrical contacts, batteries, photographic and imaging industry, brazing alloys, silverware, medical products, as coinage metal, jewelry, chemistry laboratories, catalysis, and ineffaceable inks [1, 2]. These industries release significant amount of silver which deteriorate and adversely affect the aquatic ecosystem. Silver ions can accumulate in living organisms through food chain system thus causing various diseases. The toxic effects of silver in biotic systems have been reported elsewhere [3, 4]. Being precious metal the silver ions must be removed from industrial effluents prior to their disposal into water bodies. Thus an efficient method is required for the removal or recovery of silver ion from industrial waste solutions due to the economical and environmental points of view.

Several treatment processes for the removal of silver ions from aqueous solutions have been reported such as reduction [5], ion exchange resins [6], solvent extraction [7] and adsorption [8]. The adsorption process under certain conditions has a definite edge over other methods due to its simplicity, high enrichment factor, high recovery, rapid phase separation, low cost and ability to couple with different detection techniques in on-line and off-line modes.

The adsorption of silver on various inorganic materials and organic compounds has been reported. The inorganic sorbents used for silver are activated carbon [8], titanium dioxide [9], montmorillonite [10], perlite [11], coal [12], silica gel [13], whereas the organic sorbents include polyurethane foam [14] and polymers [15]. However, some of these are either expensive, time consuming or inefficient in reducing the metal ion concentration in the effluents. Therefore, there is a need to look into other inexpensive, rapid and efficient methods for this purpose.

The adsorption capacity of an adsorbent for a specific metal ion depends upon various factors like nature of adsorbent, oxidation state of the

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adsorbate, equilibration time and pH of the adsorption medium. Equilibrium relationships between sorbents and sorbates are described by sorption isotherms which give the capacity of a sorbent for a sorbate [16]. Isotherms can be obtained by examining batch reactions at fixed temperatures.

The present work deals with a series of experiments to assess the ability of rice husk to remove silver ions from aqueous solutions as an adsorbent. Rice husk contains 15-22 % SiO_2 in hydrated amorphous form like silica gel, cellulose and lignin [17] and seems to have the potential to bind metal ions. Therefore, naturally occurring agricultural solid waste material rice husk was selected to study the silver ions adsorption capacity using Langmuir isotherm method. Linear regression was used to determine the best – fitting isotherm.

2. Experimental Procedure

2.1. Equipment

The absorption measurements were made with a Hitachi model Z-2000 polarized Zeeman atomic absorption spectrophotometer. The instrument has a strong magnetic field across the burner which provides a double-beam optical correction system. A water cooled, premix, fish-tail type burner, having a slot of 100 × 0.5 mm, was used for the air-acetylene flame. Hollow cathode lamp of silver from Hitachi was used as a radiation source.

2.2. Reagents

The husk of basmati rice was obtained from a rice mill. The husk was thoroughly washed with water to remove all dirt and was oven dried at 80°C till constant weight. The dried husk was stored in a precleaned air tight container and used as such without any physical or chemical pretreatment.

Stock solution of silver (1000 mg L^{-1}) was prepared by dissolving 0.1 gram of specpure metal (Johnson and Mathey) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 mL with water. Standard solutions were prepared by appropriate dilution of this stock solution. Fresh working standards were made immediately before use. Distilled and deionized water was used throughout.

2.3. Sorption Measurements

Known amount of rice husk was taken in a 35 mL culture tube with a screwed polyethylene cap alongwith 10 mL of standard acid solution. A fixed amount of stock solution of silver was pipetted into it. The contents were equilibrated on a mechanical wrist-action Vibromatic shaker for 15 minutes. The aqueous phase was separated and the amount of silver was determined in the solutions before and after equilibrium by flame atomic absorption spectrophotometry at 328.1 nm and using other optimized instrumental parameters (Table 1). A blank solution without metal was also prepared and treated similarly. All experiments were conducted in triplicate at ambient temperature (296 ± 1 K).

Table 1. Optimized instrumental parameters used for the determination of silver by AAS.

Parameters	Values
Lamp Current (mA)	7.0
Resonance Abs. Line (nm)	328.1
Width of Slit (nm)	1.3
PMT Voltage (v)	330
Burner Type	Standard*
Burner Height (mm)	7.5
Fuel (C_2H_2) flow (L min^{-1})	2.0
Oxidant (Air) flow (L min^{-1})	15.0

* See experimental

The percentage sorption of silver ions from the solution was calculated using the following relationship:

$$\%\ \text{Adsorption} = \frac{C_{In} - C_{Eq}}{C_{In}} \times 100 \qquad (1)$$

where C_{In} = initial concentration of metal in the solution (mol L^{-1})

C_{Eq} = concentration of metal in solution after equilibrium (mol L^{-1})

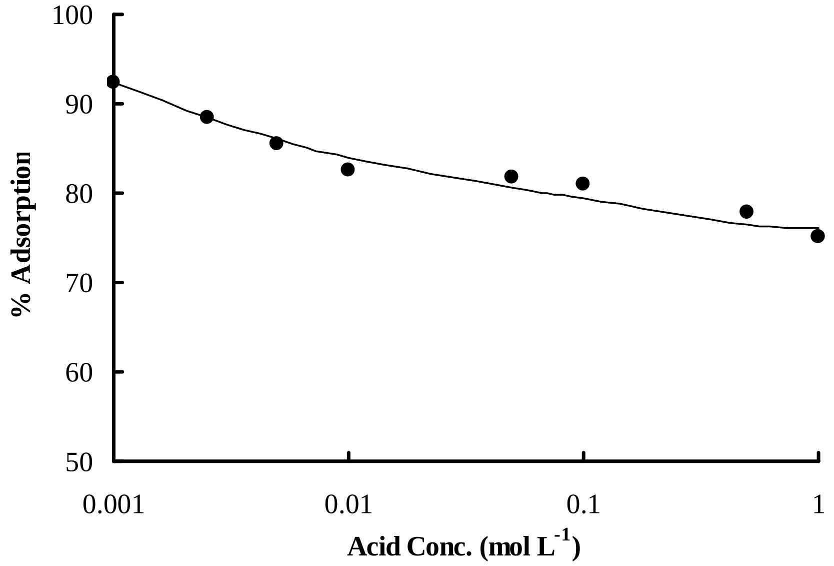

Figure 1. Effect of acid concentration on the percent adsorption of silver ions on rice husk.

3. Results and Discussion

The adsorption of silver ions from aqueous solutions on rice husk was studied by optimizing nitric acid concentration using 0.5 g of adsorbent for 10 mL of 9.271 × 10^{-5} mol L^{-1} silver concentration, using batch method and employing atomic absorption spectrophotometry. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. All the reported results are the average of at least triplicate independent measurements with an expected error of within ± 4.1 %.

3.1. Effect of Acid Concentration

The adsorption behavior of 9.271 × 10^{-5} mol L^{-1} of silver ions was checked in nitric acid solutions having a concentration range from 0.001 to 1.0 mol L^{-1} using 0.5 g of rice husk with equilibration time of 15 minutes. The concentration of silver, equilibration time and amount of rice husk were selected arbitrarily and the results are presented in Fig. 1 which shows that maximum adsorption (92.34 %) of silver ions was observed at 0.001 mol L^{-1} of nitric acid. With further increase in acid concentration the adsorption of silver was started decreasing upto 1.0 mol L^{-1}. The decrease in adsorption of silver ions at higher acid concentration may be attributed to the competition between the excess of H^+ ions in the medium and positively charged silver ions. Since maximum adsorption of silver ions was occurred from 0.001 mol L^{-1} HNO_3 solution, therefore, this acid concentration was used in all the subsequent experiments.

3.2. Effect of Ag^+ Concentration

Concentration dependence of silver ions adsorption on rice husk was studied under the optimized conditions 0.001 mol L^{-1} of acid concentration, equilibration time of 15 minutes and 0.5 g of adsorbent. The initial sorptive concentration of silver was varied from 1.854 × 10^{-4} to 1.159 × 10^{-3} mol L^{-1} and the results are shown in Fig. 2, which indicates that the percentage adsorption decreases from 91.88 to 59.30 %, with the increase in the initial silver ion concentration. The lower adsorption of silver with the increase in silver concentration may be explained on the basis of limited number of binding sites in a fixed amount of adsorbent as compared to higher concentration of metal ion.

3.3. Adsorption Isotherm

The adsorption data of Ag^+ on rice husk was subjected to Langmuir isotherm model [18]. The Langmuir model represents chemisorption on a set of well defined localized adsorption sites having the same sorption energies independent of surface coverage and no lateral interaction between adsorbed molecules. Maximum sorption capacity

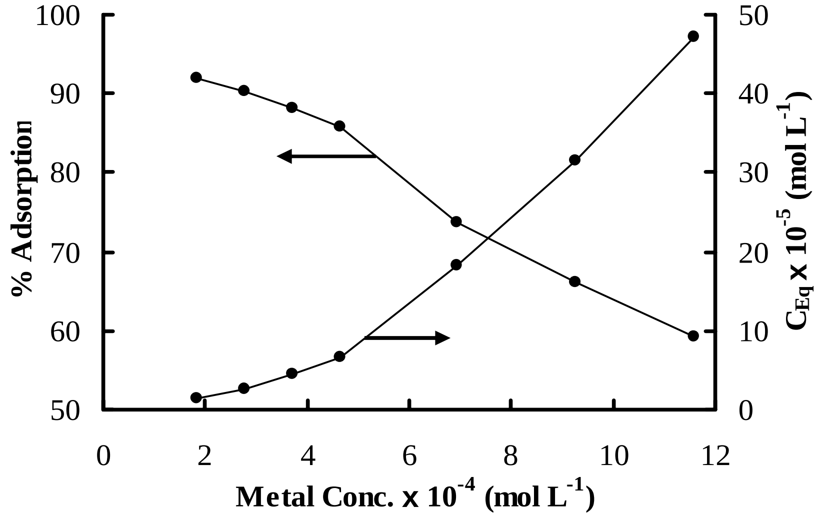

Figure 2. Adsorption variation and equilibrium concentration of silver ions as a function of its own concentration on rice husk.

(Q_m) indicates monolayer coverage of sorbent with sorbate (K_L) and relates to enthalpy of sorption. The Langmuir model may be written as:

$$C_{Ad} = \frac{Q_m K_L C_{Eq}}{1 + K_L C_{Eq}} \qquad (2)$$

The linearized form of equation (2) is:

$$\frac{C_{Eq}}{C_{Ad}} = \frac{1}{K_L Q_m} + \frac{C_{Eq}}{Q_m} \qquad (3)$$

where

C_{Ad} = amount of metal ions adsorbed (mol g^{-1})

C_{Eq} = equilibrium concentration of metal ions in solution (mol L^{-1})

Q_m = adsorption capacity of metal ions (mol g^{-1})

K_L = constant

In general Q_m and K_L are functions of pH, ionic media and ionic strength. The values of Q_m of silver ions may be computed graphically by using the linear equation (3). A straight line was obtained by plotting C_{Eq}/C_{Ad} against C_{Eq} for silver ions adsorption on rice husk with slope equal to $1/Q_m$, and intercept equal to $1/K_LQ_m$. The Langmuir plot for Ag^+ ions adsorption on rice husk is shown in Figure 3. The data revealed that the Langmuir adsorption model was obeyed over the entire concentration range studied. The values Q_m and K_L for Ag^+ ions were calculated from the slopes and intercepts of Langmuir plot and were found to be $(1.504 \pm 0.054) \times 10^{-2}$ m mol g^{-1} and $(16.578 \pm 2.227) \times 10^3$ dm^3 mol^{-1}, respectively.

Three other linearized equations of Langmuir isotherm are:

$$\frac{1}{C_{Ad}} = \left(\frac{1}{K_L Q_m}\right)\frac{1}{C_{Eq}} + \frac{1}{Q_m} \qquad (4)$$

$$C_{Ad} = Q_m - \left(\frac{1}{K_L}\right)\left(\frac{C_{Ad}}{C_{Eq}}\right) \qquad (5)$$

$$\frac{C_{Ad}}{C_{Eq}} = K_L Q_m - K_L (C_{Ad}) \qquad (6)$$

where

C_{Ad} = amount of metal ions adsorbed (mol g^{-1})

C_{Eq} = equilibrium concentration of metal ions in solution (mol L^{-1})

Q_m = adsorption capacity of metal ions (mol g^{-1})

K_L = constant

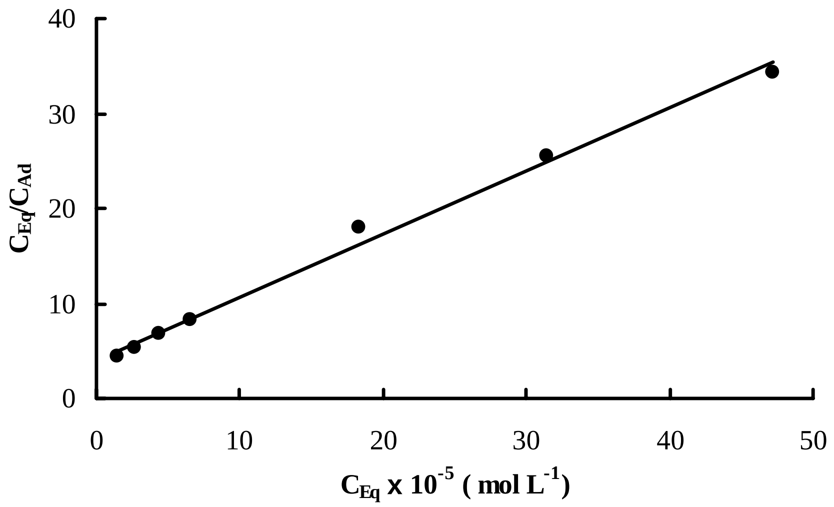

Figure 3. Langmuir adsorption isotherm (Type 1) of silver ions on rice husk.

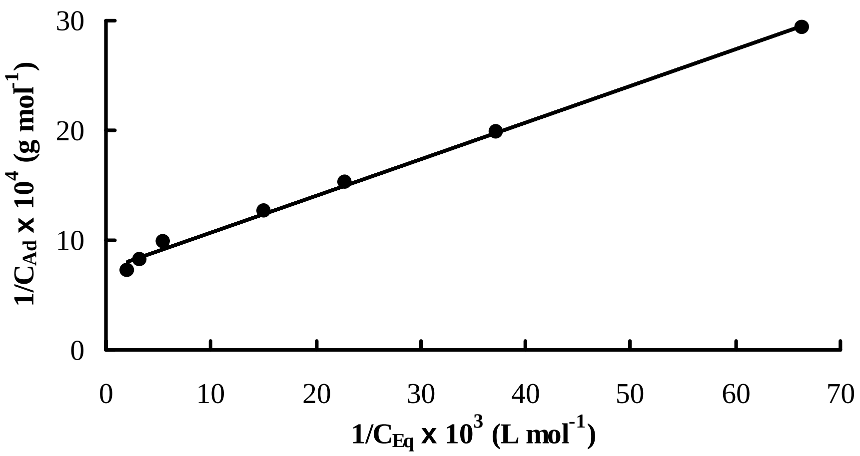

Figure 4. Langmuir adsorption isotherm (Type 2) of silver ions on rice husk.

The Langmuir plots for Ag^+ ions adsorption on rice husk for different types of linearized equations (No. 4-6) are shown in Figures 4-6, whereas the determined parameters (Q_m, K_L and R^2) are reported in Table 2. The determined adsorption capacities of silver ions on rice husk from 1-4 types of Langmuir isotherm equations were found to be 1.62, 1.47, 1.08 and 1.54 mg g^{-1}, respectively. The data in Table 2 indicate that the calculated/ determined parameters from all the four types of linear forms of Langmuir isotherm are comparable and are within the statistical variations, thus confirming the applicability of the adsorption data of silver ions on rice husk. The high value of correlation coefficient (R^2) obtained from Eq. 4 indicates better fit of the equation as compared to rest of the three forms.

3.4. Effect of Isotherm shape

The effect of isotherm shape can be used to predict whether an adsorption system is "favorable" or "unfavorable". By using the essential characteristics of the Langmuir isotherm, it can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter "R_L" which is defined by the following relationship [19].

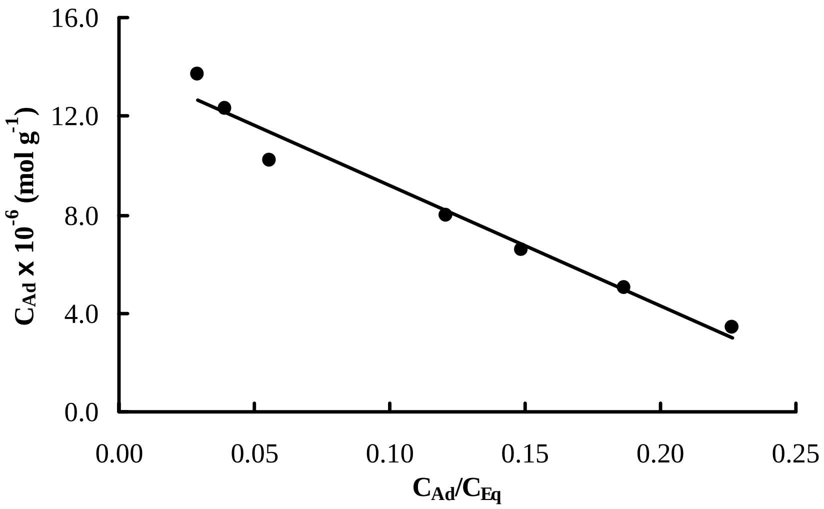

Figure 5. Langmuir adsorption isotherm (Type 3) of silver ions on rice husk.

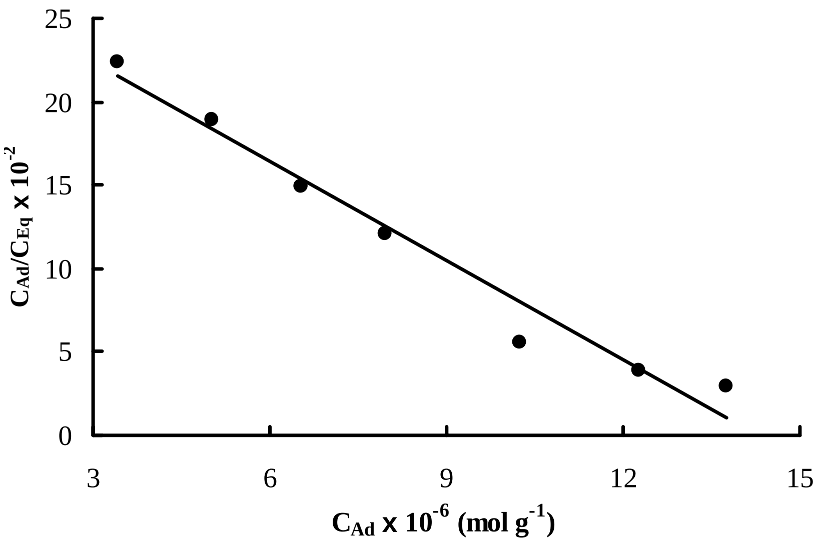

Figure 6. Langmuir adsorption isotherm (Type 4) of silver ions on rice husk.

Table 2. Determined Langmuir constants of different equations for the adsorption of silver ions on rice husk.

Langmuir Isotherm	Plot	Equation	Q_m (mol g^{-1})	K_L (Lmg^{-1})	R^2
Type 1	C_{Eq}/C_{Ad} Vs C_{Eq}	y = 66472 x + 4.0097	1.50×10^{-5}	16578	0.9937
Type 2	$1/C_{Ad}$ Vs $1/C_{Eq}$	y = 3.3499 x + 73243	1.36×10^{-5}	21864	0.9967
Type 3	C_{Ad} Vs (C_{Ad}/C_{Eq})	y = - 5.0×10^{-5} x + 1.0×10^{-5}	1.0×10^{-5}	20000	0.9688
Type 4	C_{Ad}/C_{Eq} Vs C_{Ad}	y = -19860 x + 0.2832	1.43×10^{-5}	19860	0.9688

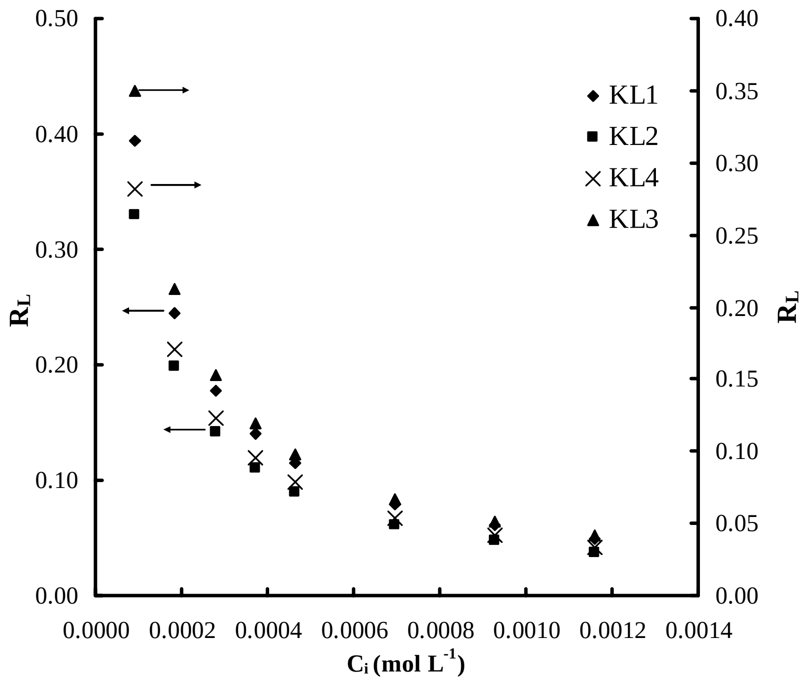

Figure 7. Variation of R_L values as a function of initial concentration of silver ions.

$$R_L = \frac{1}{(1 + K_L C_{In})} \quad (7)$$

where

C_{In} = Initial concentration of metal ion (mol L^{-1})

K_L = the Langmuir constant related to adsorption energy (L mg^{-1})

R_L = a dimensionless separation factor

The relationship between determined R_L and C_{In} for the adsorption of silver ions on rice husk, calculated by using the Langmuir constants KL1, KL2, KL3 and KL4 for the four Langmuir equations are shown in Fig. 7 to show the essential features of the Langmuir isotherm. The R_L value implies the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) [20]. All the determined values of separation factor shown in Fig. 7 are in the range of 0.038 to 0.394, indicating favorable adsorption of silver ions onto the rice husk, under the conditions used for the experiments.

3.5. Comparison of the Adsorption Capacities

The maximum determined adsorption capacity of silver ions on rice husk (1.62 mg g^{-1}) was also compared with the already reported values in literature for different adsorbents and are given in Table 3. The maximum determined adsorption capacity is higher than the reported value for silica gel and montmorillonite, comparable to that of coal, and is lower than those of perlite, polymer and polyurethane foam.

Table 3. Comparison of adsorption capacity of silver on different adsorbents .

No.	Adsorbent	Capacity (mg g^{-1})	Reference
1	Montmorillonite	1.31	[10]
2	Perlite	8.46	[11]
3	Coal	1.87	[12]
4	Silica gel	0.38	[13]
5	Polyurethane foam	16.18	[14]
6	Polymers	2.41	[15]
7	Rice husk	1.62	Present study

4. Conclusions

Naturally occurring agricultural solid waste i.e., rice husk proved to be a good adsorbent for silver ions from nitric acid media. The adsorption process seems to be rapid and efficient and may be utilized for the recovery of silver metal ions from aqueous solutions. The adsorption data obeys the Langmuir isotherm model. Determined adsorption capacity of rice husk by Langmuir isotherm method is comparable or better than the values reported for other adsorbents.

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