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# Multi metal ion sorption capacity of watermelon rind extract capped ZnS nanoparticles

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**Abstract**

The present study reports the use of watermelon rind extract capped ZnS nanoparticles (W-ZnS) as potential adsorbent for the removal of heavy metal ions such as $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions from aqueous solution. Batch adsorption studies were employed by varying the parameters such as pH, contact time, adsorbent dose, temperature and initial metal ion concentration. The maximum loading capacity of W-ZnS was found to be 106.4, 69.7 37.7, 40.2 and 32.8 mg $g^{-1}$ respectively for $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions. Two well know kinetic models were employed and found that pseudo second order model fits well to the kinetic data. Thermodynamic data reveals that removal of $Pb^{2+}$,

$Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ ions are spontaneous and exothermic in nature. These results conclude that acid W-ZnS is a potential adsorbent for the removal of heavy metal ions from aqueous solution..

***Key Words*:**Watermelon rind; ZnS; Adsorption; Heavy metal ions.

# 1 INTRODUCTION

Rapid industrialization has resulted in the increased disposal of effluents loaded with heavy metals and organic contaminants. Industries such as electroplating and battery manufacturer's discharge huge amount of effluents into environment loaded with high concentrations of heavy metal ions [1,2]. The presence of heavy metals in drinking water can cause damage to nervous system, lungs, kidneys and liver. Hence, treatment of industrial effluents loaded with heavy metal ions is desirable.

Various treatment techniques are developed by many researchers for the remediation or removal of heavy metal ions from aqueous solution [3]. Among the techniques, adsorption was found to be the most efficient, rapid and economical treatment technique for the removal and recovery of heavy metal ions from wastewater [4,5]. Activated carbon was found to be the most efficient adsorbent for the removal of heavy metal ions. The efficiency exhibited by activated carbon is mainly due to presence of ample micropore and misopore volume and high surface areas [3]. However, the cost of activation and regeneration of used carbon limits the application in commercial stage. Hence the researchers are in search of new alternative sorbents for the removal of heavy metal ions from aqueous solution.

Nano adsorbents are new class of materials with potential application in removal of heavy metal ions and synthetic dyes from aqueous solution. Nano adsorbents exhibit higher sorption capacity due to its high surface area and small size. Qu et al., summarized the potential applicability of various nano adsorbents in water and wastewater treatment in a review [6]. Semiconductor nanoparticles (NP's) in the size ranging from 1-10 nm have received much interest because of their unique properties. Among II-VI semiconductors NP's, Zinc Sulphide (ZnS) was considered to

be an important material which has a wide band gap 3.5 eV for cubic phase at room temperature. The ZnS NP's are well known for its photocatalytic activity towards synthetic dyes [7]. The potential of ZnS NP's towards the removal of heavy metal ions are yet to be explored. In view of this, the present study deals with the application of watermelon rind extract capped ZnS NP's as adsorbent for the removal of heavy metal ions from aqueous solution.

# 2 EXPERIMENTAL METHODS

*Preparation of Nano adsorbent*

The Watermelon rind extract capped ZnS nanoparticles was synthesized according to the procedure reported by Lakshmipathy et al,. [7]. The synthesized ZnS NP's was characterized with TEM to confirm the formation of ZnS NP's (Fig.1)

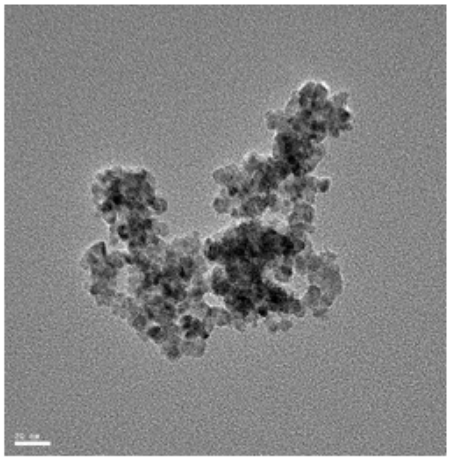

Fig. 1 TEM micrograph of ZnS NP's

*Batch adsorption studies*

Batch adsorption experiments were conducted at room temperature (30±1) in a Roto spin unit at 50 rpm using 50 ml torson tubes. Effect of adsorption parameters such as adsorbent dose, contact time, pH and initial adsorbate concentration were studied. Effect of pH on adsorption was evaluated by varying pH

from 2-8 using 0.1M HCl and 0.1M NaOH for adjustments. The contact time was varied between 10 to 120 min to study the effect of time on sorption and the adsorbent dosage was varied from 0.5 g $L^{-1}$ to 5 g $L^{-1}$ to know the effect of dosage. For each parameter study the solid phase was separated using centrifugation at 5000 rpm for 5 min and the residual concentration present in the supernatant was determined from Atomic Absorption spectrophotometer (AAS). A blank run without adsorbent was carried out in order to determine the adsorption of metal ions es onto walls of the tubes. The amount of metal ions adsorbed to ZnS NP's was determined from Eq. (1) and % removal was evaluated by Eq (2).

$$q_e = (C_0 - C_1)\,\frac{V}{M} \text{.....(1)}$$

$$\%Removal = \frac{C_0 - C_1}{C_0} x100 \text{.....(2)}$$

Where $q_e$ is the metal or dye uptake (mg $g^{-1}$), $C_o$ and $C_1$ are initial and final metal or dye concentrations ($mg^{-1}L$), V is the solution Volume (L), and M is the mass of the adsorbent (g)

# 3 Results and discussion

*Effect of pH*

It is well known and extensively reported that pH is an important variable governing the adsorption of metal ions by adsorbent [8,9]. The solution pH influences metal ion sorption on to active sites of adsorbent due to competition between the metal and $H^+$ ions. Thus, the batch equilibrium studies were conducted at different initial pH values in the range of 2-8. It was observed that very little metal ions sorption took place at pH 2. A continuous increase in the sorption capacity of ZnS NP's occurred in the range of pH 2-6. Maximum removal efficiency was observed at pH 5 for $Pb^{2+}$ and $Cd^{2+}$ ions and at pH 6 for $Ni^{2+}$ $Cu^{2+}$ and $Co^{2+}$ ions. At pH 2 the low metal sorption may be explained on the basis of protonation of active sites by H+ ions. The increase in metal sorption with increase in pH can be explained in terms of pHpzc (point zero charge) of the adsorbent and metal speciation

occurring in the solution [10-12].

*Kinetics of adsorption*

Kinetic experiments were carried out identical to the equilibrium studies. The aqueous samples were taken at preset time intervals and concentrations of metal ions were similarly measured. It was observed that removal rate of metal ions by ZnS NP's was extremely rapid in first 20 min and reached equilibrium within 30 min. The rapid removal in first 20 min is due to immediate availability of more number of active sites at surface for adsorption. To examine the rate controlling mechanism of present process, such as mass transfer and chemical reaction, the pseudo first order and pseudo second order kinetic models was used to test the experimental data of dye at different initial dye concentrations.

The pseudo first order rate equation of Lagergren is represented as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{.....(3)}$$

Where $q_e$ is the amount of metal ion adsorbed at equilibrium (mg $g^{-1}$), $q_t$ is the amount of metal ion adsorbed at time t and $k_1$ is the first order reaction rate constant.

Based on the sorption equilibrium capacity pseudo second order equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \text{.....(4)}$$

Where $k_2$ (g $mg^{-1}$ $min^{-1}$) is the rate constant of pseudo second order adsorption. The values of $k_2$ and $q_e$ can be calculated from the plot of $\frac{t}{q_t}$ versus t.

The respective parameters and correlation coefficients derived from plots are summarized in Table 1. It was observed that pseudo first order kinetic model failed to fit well to the obtained kinetic data. The failure of the model is further supported by low correlation coefficients and theoretical loading capacity values obtained from plots. These observations suggest that the removal of heavy metal ions by ZnS NP's

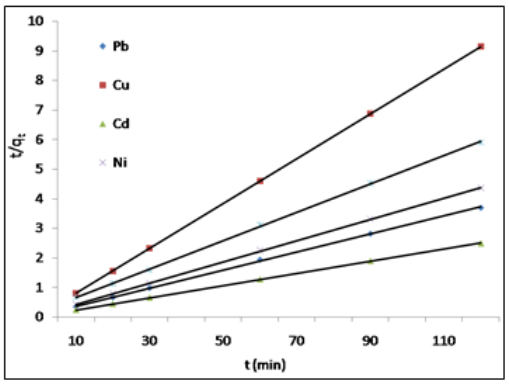


Fig. 2 Plots of pseudo second order kinetic model for the removal of metal ions by ZnS NP's from aqueous solution

Table 1. Kinetic constants derived from plots of pseudo first order and pseudo second order kinetic models for the removal of metal ions by ZnS NP's

| Model | Parameter | Pb | Cu | Cd | Ni | Co |
|---|---|---|---|---|---|---|
| Experimental | $q_e$ (mg g$^{-1}$) | 29.9 | 16.8 | 28.9 | 16.6 | 11.5 |
| Pseudo first order | $q_e$ (mg g$^{-1}$) | 6.54 | 4.32 | 5.67 | 5.01 | 0.78 |
| | $k_1$ (min$^{-1}$) | -0.115 | -0.286 | 0.323 | -0.286 | -0.321 |
| | $R^2$ | 0.852 | 0.986 | 0.980 | 0.967 | 0.971 |
| Pseudo second order | $q_e$ (mg g$^{-1}$) | 30.1 | 17.2 | 27.9 | 16.9 | 12.2 |
| | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.041 | 0.045 | 0.056 | 0.043 | 0.439 |
| | $R^2$ | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 |

does not follow pseudo first order kinetic model. The data was found to fit well to pseudo second order kinetic model (Fig.2). The applicability of pseudo second order kinetic model to the experimental data obtained for ZnS NP's is supported by theoretical loading capacity values and correlation coefficients. The correlation coefficients obtained were close to one for all the metal ions adsorption onto ZnS NP's. The theoretical loading capacity values derived from plots are very close to calculated experimental values obtained from kinetic experiments for the removal of metal ions by ZnS NP's. These observations suggest that the adsorption of metal ions onto ZnS NP's follows pseudo second order kinetic model.

According to pseudo second order, boundary layer resistance is not the rate-limiting step, the external resistance model cannot

adequately describe the adsorption mechanism, and the process controlling the rate may be a chemical sorption involving valences forces through sharing or exchanging of electrons between sorbate and sorbent [13].

*Adsorption isotherms*

In order to evaluate the maximum adsorption capacity of ZnS NP's for metal ions, the ZnS NP's were allowed to contact with varying concentration (50-300mg/L) of metal ion solutions at equilibrium. It was observed that the loading capacity of ZnS NP's increased with increase in the initial concentration and the maximum loading capacity was found to be 106.4, 69.7 37.7, 40.2 and 32.8 mg $g^{-1}$ respectively for $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions. In order to examine the relationship between the concentration of metal ions at equilibrium ($Ce$) and$_m etal loading capacity (q_e)$ various isotherm models were employed for the experimental data.

Freundlich isotherm is an empirical equation that is based on the sorption of an adsorbate on a heterogeneous surface of an adsorbent. The linear form of Freundlich isotherm is given as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \text{.....(5)}$$

Where $K_f$ and n are Freundlich constants indicate the adsorption capacity and intensity, respectively. If Eq (3) applies, a plot of log $q_e$ versus log $C_e$ will give a straight line.

The Langmuir isotherm assumes monolayer adsorption process and linear form of Langmuir isotherm after rearrangement is given as

$$\frac{C_e}{q_a} = \frac{1}{bV_m} + \frac{C_e}{V_m} \text{.....(6)}$$

Where $C_e$ is the concentration of metal ions at equilibrium ($mg^{-1}$), $q_e$ is the amount of metal adsorbed per unit mass of adsorbent (mg $g^{-1}$), $V_m$ is the amount of adsorbate at complete monolayer coverage (mg $g^{-1}$), and b is a constant that relates to the heat of adsorption (L $mg^{-1}$).

The Langmuir and Freundlich constants and respective

correlation coefficients derived from the plots for the removal of of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions by ZnS NP's are represented in Table. 2. It was observed that equilibrium data tend to fit well to both Langmuir and Freundlich isotherms except for $Co^{2+}$ ions. The correlation coefficients obtained for both the models were also close to one suggesting that both Langmuir and Freundlich models are applicable for the removal of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ ions In case of $Co^{2+}$ ions, the Langmuir isotherm found to have better fit compared to Fruendlich isotherm. The better fit of Langmuir isotherm is further supported by its correlation coefficients. The theoretical monolayer coverage ($V_M$) derived from plots of Langmuir isotherm were close to the calculated experimental values suggesting the applicability of Langmuir isotherm to of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions. These results suggest that adsorption of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ ions onto ZnS NP's is multilayer and each layer obeys Langmuir isotherm.

Table 2 Freundlich and Langmuir isotherm parameters calculated for the removal of heavy metals from aqueous solution by ZnS NP's (Time 30 min and Temperature 303K)

| Metal ions | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|
| | $K_f$ | 1/n | $R^2$ | $V_m$(mg $g^{-1}$) | b (L $mg^{-1}$) | $R^2$ |
| Pb | 4.04 | 0.02 | 0.993 | 105.6 | $5.9x10^{-4}$ | 0.986 |
| Cd | 3.7 | 0.02 | 0.979 | 71.1 | $1.4x10^{-3}$ | 0.992 |
| Cu | 3.3 | 0.02 | 0.963 | 39.2 | $1.5x10^{-4}$ | 0.999 |
| Ni | 3.6 | 0.01 | 0.970 | 43.4 | $8.3x10^{-4}$ | 0.962 |
| Co | 1.6 | 0.04 | 0.915 | 40.4 | $3.7x10^{-4}$ | 0.988 |

Table 3 Thermodynamic parameters derived for the removal of heavy metal ions from aqueous solution by ZnS NP's (Time 30 min and Initial concentration 50mg $L^{-1}$)

| Metal ions | Temperature (K) | Loading capacity (mg $g^{-1}$) | $\Delta G^{\circ}$ (KJ $mol^{-1}$) | $\Delta H^{\circ}$ (KJ $mol^{-1}$) | $\Delta S^{\circ}$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|
| $Cd^{2+}$ | 303 | 30.1 | -4.610 | -4.150 | 447.5 |
| | 313 | 30.4 | -5.022 | | |
| | 323 | 30.7 | -5.505 | | |
| $Ni^{2+}$ | 303 | 26.2 | -2.267 | -2.065 | 247.7 |
| | 313 | 26.6 | -2.498 | | |
| | 323 | 26.8 | -2.685 | | |
| $Pb^{2+}$ | 303 | 31.8 | -6.600 | -6.064 | 553.1 |
| | 313 | 32.0 | -7.208 | | |
| | 323 | 32.1 | -7.707 | | |
| $Cu^{2+}$ | 303 | 26.8 | -2.493 | -2.328 | 209.4 |
| | 313 | 27.0 | -2.706 | | |
| | 323 | 27.1 | -2.846 | | |
| $Co^{2+}$ | 303 | 12.8 | 2.242 | 2.477 | -275.9 |
| | 313 | 14.2 | 1.847 | | |
| | 323 | 14.8 | 1.691 | | |

*Thermodynamics of adsorption*

The adsorption of metal ions on to ZnS NP's was studied at three different temperatures in the range of 303-323 K. From the experimental results, thermodynamic parameters including the change in free energy ($\Delta G^{\circ}$), enthalpy ($\Delta H^{\circ}$) and entropy ($\Delta S^{\circ}$) were used to describe the thermodynamic behavior of soprtion of metal ions onto ZnS NP's.

Thermodynamic parameters can be evaluated from the following equations

$$K_D = \frac{q_e}{C_e} \text{.....(7)}$$
$$\Delta G^{\circ} = -RT \ln K_D \text{.....(8)}$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \text{.....(9)}$$

Where $K_D$ is the equilibrium constant, $q_e$ is the amount of metal ions adsorbed, $C_e$ is the equilibrium concentration in solution (mg/L), R is the gas constant (8.314 J/Mol/K), T is the temperature (K), $\Delta H^{\circ}$ is enthalpy and $\Delta S^{\circ}$ is entropy.

The thermodynamics parameters derived from experimental data are represented in Table 3. The change in free energy ($\Delta G^{\circ}$) values was found to be negative for all metal ions except $Co^{2+}$ ions suggesting that removal of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ ions are

spontaneous and $Co^{2+}$ ions is non-spontaneous in nature by ZnS NP's. The negative values of $\Delta G^\circ$ found to increase with increase in temperature depicting the more spontaneous nature of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ ions removal at higher temperatures by ZnS NP's. The positive values of $\Delta G^\circ$ tend to decrease with increase in temperature suggesting decrease in non-spontaneous nature of Co2+ ions removal by ZnS NP's. The negative and positive values of H indicate that removal of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ is exothermic and Co2+ ions is endothermic in nature. The positive S values of ZnS NP's towards $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Co^{2+}$ ions indicate the increase in randomness of solid-liquid interface during the sorption.

# 4 CONCLUSION

The ZnS NP's was synthesized and explored for the multi metal sorption from aqueous solution. ZnS NP's exhibited highest loading capacity and preferential uptake towards $Pb^{2+}$ ions and least towards $Co^{2+}$ ions respectively. All the selected heavy metal ions in the study showed highest removal efficiency at pH 5 and 6. The kinetic studies reveal that removal of heavy metal ions by ZnS NP's follows pseudo second order kinetic model. Thermodynamic parameters suggested that the removal of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Ni^{2+}$ ions is spontaneous and exothermic and $Co^{2+}$ ions is non spontaneous endothermic in nature. These results conclude that ZnS NP's are superior adsorbent for the removal of heavy metal ions from aqueous solution.

# References

[1] F. Fu, Q. Wang. "Removal of heavy metal ions from wastewaters: A review." J. Environ. Manage. Vol. 92 pp. 407-418, 2011.

[2] A. Demirbas. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review" J. Hazard. Mater. Vol. 167, pp. 1-9, 2009.

[3] W.S.W. Ngah, M.A.K.M. Hanafiah. "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review" Bioresour Technol. Vol. 99 pp. 3935-3945, 2008.

[4] A. Srinivasan, T. Viraraghavan. "Decolorization of dye wastewaters by biosorbents: a review" J. Environ. Manage. Vol. 91 pp. 1915-1929, 2010.

[5] E. Forgacs, T. Cserhati, G. Oros. "Removal of synthetic dyes from wastewaters: a review". Environ. Int. vol. 30, pp. 953-971, 2004.

[6] X. Qu, J.J. Alveraz, Q. Li. "Applications of nanotechnology in water and wastewater treatment". Wat Res. Vol. 47, pp. 3931-3946, 2007.

[7] R. Lakshmipathy and N.C. Sarada. "Application of watermelon rind as sorbent for removal of nickel and cobalt from aqueous solution". Int. J. Miner. Process. Vol. 122, pp. 63-65, 2013

[8] M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, "Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste". J. Poch. J. Hazard. Mater. Vol. 133 pp. 203-211, 2006

[9] S. Karthikeyan, R. Balasubramanian, C.S.P. Iyer. "Evaluation of the marine algae Ulva fasciata and Sargassum sp". For the biosorption of Cu(II) from aqueous solutions Bioresour. Technol., Vol. 98, pp. 452-455, 2007.

[10] A. Jang, Y. Seo, P.L. Bishop. "The removal of heavymetals in urban runoff by sorption on mulch". Environ. Pollut. Vol. 133, pp. 117-127, 2005

[11] R. Jayachandra, R. Lakshmipathy, S.R. Reddy. "Hydrophobic D-galactose based ionic liquid for the sequestration of Pb2+ ions from aqueous solution". J. Mol Liquid, vol. 219, pp. 1172-1178, 2016

[12] R. Lakshmipathy and N.C. Sarada. "Metal ion free watermelon (Citrullus lanatus) rind as adsorbent for the removal of lead and copper ions from aqueous solution". Desalin. Wat Treat, vol. 57 pp. 15362-15372, 2016

[13] R. Lakshmipathy, N.C. Sarada. "Methylene blue adsorption onto native watermelon rind: batch and fixed bed column studies". Desalin. Wat Treat, Vol. 57, pp. 10632-10645, 2016