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COMPARATIVE STUDIES OF EXTRACTIVE CAPACITYOF SILVER NANOPARTICLES AND SCHIFF BASE COATED SILVER NANOPARTICLES FOR Pb (II), Cd (II) AND Zn (II) FROM CONTAMINATED WATER USING AAS

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ABSTRACT

The present study deals with, two adsorbents were compared for extractive capacity of Pb (II), Cd (II) and Zn (II) from contaminated water. The first adsorbent silver nanoparticles were prepared by using the chemical reduction method and second adsorbent silver nanoparticles modified with Schiff base was prepared in two steps. First, Schiff base was prepared by condensation of 2-hydroxy-1-napthaldehde with 4-amino-antipyrine and next silver nanoparticle modified with a Schiff base by suitable method using above prepared silver nanoparticles and Schiff base. The synthesized adsorbents were characterized by elemental analysis, UV-VIS, FTIR, and SEM analysis. Peanut shells were used as a solid phase for remediation of metal ions by column method. Several parameters were examined such as initial metal ion concentration, p^H, contact time and adsorbent weight. The maximum adsorption capacity for Pb (II) = 161.29, Cd (II) = 64.10 and Zn (II) = 384.61 respectively, for AgNPs@SB and Pb (II) = 64.10, Cd (II) = 61.34 and Zn (II) = 99 respectively, for silver nanoparticles. Comparing both adsorbents, obtained results indicate that second adsorbent silver nanoparticles modified Schiff base is more efficient than first adsorbent unmodified silver nanoparticles. The examined data showed that removal of each metal ions follows Langmuir adsorption isotherm on both adsorbents.

Keywords: Extractive capacity, Schiff base, Silver nanoparticles, Adsorbent

1. INTRODUCTION

The purification of metal ions from water samples play a key role for the remediation of environmental water sources, industrial and geological waste water **[1, 2]**. Heavy metal ions such as Pb (II) and Cd (II) have a hazardous effect because of its carcinogenic and non-biodegradable property. The possibility of inflation of heavy metal ions in human being is very high. The permissible limit of Pb (II) and Cd (II) in drinking water is 10 ug L^{-1} and 3 ug L^{-1} respectively **[3]**. Several techniques have been commonly used for the separation of the large amount of heavy metal ions in water, such as ion exchange, precipitation, adsorption, dialysis and extraction. Now a days, adsorption technique for heavy metal removal has more attractive for researchers because in this technique mostly eco-friendly materials are used and have low production cost **[4-9]**. Nanomaterial play a vital role in metal ion removal due to their physical and chemical properties. The capacity of nanosized material for the separation of biomolecules, inorganic and organic species have widely examined **[10-12]**. Nanoparticles used as a highly efficient adsorbent due to its large surface area and maximum availability of active sites for complexation with metal ions. Additionally, adsorbents which have functional groups are developed to improve the adsorption efficiency **[13]**. Schiff bases have O and N donor atom which provides high binding affinities for metal ions to form stable complex **[14-18]**. Schiff bases have hydrophilic and hydrophobic sites which can be formed complex with metal ion and can be attached to the adsorbent surface respectively. This reason will be the increase adsorption efficiency of the adsorbent **[19-20]**.

The aim of present work comparison between two adsorbents silver nanoparticles and silver nanoparticles modified with Schiff base for removal of heavy metal ion in term of adsorption capacity. Adsorption isotherm studies for the remediation of Pb (II), Cd (II) and Zn (II) on silver nanoparticles and silver nanoparticles modified with Schiff base. Langmuir and Freundlich isotherm were used to analyze experimental data.

2. EXPERIMENAL

2.1. Materials

2-hydroxy-1-napthaldehyde, 4-amino antipyrine, silver nitrate and sodium borohydride were purchased from Sigma Aldrich. Ethanol and methanol were purchased from CDH. Throughout the research work double distilled water was used. All the solvents were purified by standard method.

2.2. Synthesis of Schiff base

Schiff base was prepared by condensation of required amount of 2-hydroxy-1-

naphthaldehyde with required amount of 4-amino antipyrine in ethanolic medium and refluxed for 2-3 hours. The mixture was cooled and the precipitate was filtered and recrystallized from ethanol and petroleum ether to give purified orange-yellow compound.

Scheme of synthesis of ligand is given below in **Figure 1**.

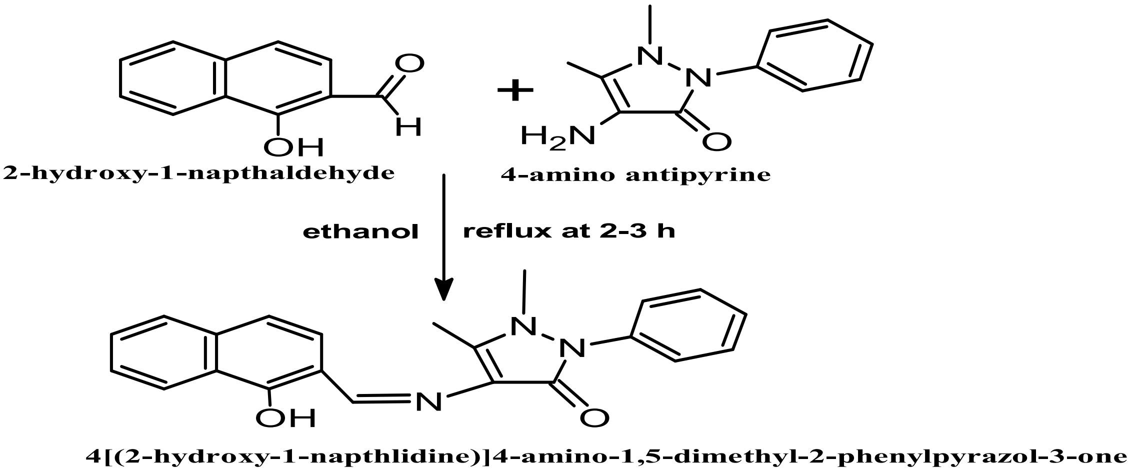

Figure 1: Synthesis of Schiff base

2.2. Synthesis of silver nanoparticles

Silver nanoparticles were prepared according to the previously reported method **[21]**. In a 250 ml conical flask pour 150 ml ice coated sodium borohydride [$NaBH_4$], then add 50 ml silver nitrate [$AgNO_3$] solution drop by drop and vigorously stir on magnetic stirrer. A dark yellow colloidal solution of silver nanoparticles was obtained.

2.3. Synthesis of Silver nanoparticles modified with Schiff base [AgNPs@SB]

AgNPs@SB was prepared according tothe previously reported method **[22]**. To the silver nanoparticles colloidal solution as prepared above, a fixed volume of Schiff base prepared above was added and stirred for 15-20 min. on magnetic stirrer. A brick red coloured precipitate was obtained. The precipitate was filtered and recrystallized from ethanol and petroleum ether.

2.4. Synthesis of solid phase

Solid phase was prepared according to the previously reported method **[23]** using peanut shells. Peanut shells were crushed and washed with 0.5% HCl and dried in oven overnight. Then grounded by mill and carbonized for 2 h. The carbonized material was soaked in NaOH in 1:1 overnight, then dried in oven for overnight and then activated for 2h. The obtaining activated carbon was washed with double distilled water, filtered and dried in oven.

2.5. Adsorption experiment

Adsorption of Pb (II), Cd (II) and Zn (II) was carried out by column method. 25 ml

Water sample containing Pb (II), Cd (II) and Zn (II) was pouring into two different conical flask and add 0.001 gm of silver nanoparticles and AgNPs@SB respectively. This mixture was pouring in the column at the desired p^H with 1 to 15 ppm concentration of sample and passed through the column with a flow rate 1.0 ml/min. The final concentration of each metal ion was determined by using FAAS from MNIT Jaipur.

The amount of adsorbed metal ion was calculated by using the following equation:-

$$q_e = \frac{V(Co - Ce)}{m}$$

Where, q_e = adsorbed amount of solute from solution in (mg/g), m = weight in gram of adsorbent in (g), V = volume of adsorbate in (L), C_O = initial metal ion concentration (mg /L) and C_e = concentration of metal ion at equilibrium (mg/L)

3. RESULT AND DISCUSSION

3.1 Characterization of Materials

3.1.1Physical properties

Physical properties of Schiff base and AgNPs@SB are shown in **Table 1**.

3.1.2 Spectral studies

Silver nanoparticles and AgNPs@SB was characterized by the UV-VIS spectra whichare shown in **Figure 2a**. The colour change of reaction mixture indicates the formation of silver nanoparticles. The UV-VIS spectra of silver nanoparticles shown plasmon band at 390 nm. According to past studies the plasmon band observed at a wavelength between 380 to 395 nm **[21]**. **Figure 2b** shows the sharp adsorption band at 470 nm while in **Figure 2a** absorption band appeared at 390 nm, which showed shifting of absorption band at higher wavelength which confirmed the formation of AgNPs@Schiff base.

The chemical composition of silver nanoparticles and AgNPs@SB were confirmed by FTIR spectra. The FTIR spectra of silver nanoparticles and AgNPs@SB was shown in **Figure 3 (a, b)**. FTIR spectral data of silver nanoparticles and AgNPs@SB was shown in **Table 2**.

Scanning electron microscope (SEM) images are used to measure the particle size. The SEM images of silver nanoparticles and AgNPs@SB are shown in **Figure 4 (a, b)**. The SEM analysis of silver nanoparticles and AgNPs@schiff base is carried out at MNIT, Jaipur. The synthesized silver nanoparticles SEM image **(Figure 4a)** shows particle size is around 50 nm. **Figure 4 (b)** shows the SEM images of AgNPs@SB shows net cross-lnked structure, which is suitable for adsorption of metal ions on surface.

3.2. Adsorption studies

3.2.1. Effect of initial concentration of metal ions

The effect of initial metal ion concentration on adsorption of metals [Pb (II), Cd (II) and Zn (II)] on AgNPs@SB and silver nanoparticleis shown in **Figure 5 (a, b)** respectively.From fig. 5 (a,b), it is observed that increasing initial concentrations of metal ion, Cd (II),Pb(II) and Zn (II) from 1 to 15 ppm. decreases the % removal of metal ions.

3.2.2 Effect of p^H

The effect of p^H on water sample is investigated at different p^H values from 2 to 10 with constant parameter: initial metal ion concentration of metals [Pb (II) = 2 ppm, Cd (II) = 1 ppm and Zn (II) = 3 ppm], contact time (20 min.) and adsorbent weight (.005 gm) on silver nanoparticles and AgNPs@SB is shown in **Figure 6 (a,b)**.

The optimum p^H obtained for the metal ions Pb(II), Cd(II) and Zn(II) are 8, 6 and 4respectively. **Figure 6 (a, b)** showed that the adsorbents silver nanoparticles and AgNPs@SB absorbed the metal ions in following order Zn (II) > Pb (II) > Cd (II).

3.2.3 Effect of contact time

The effect of contact time on metal ions Pb (II), Cd(II) and Zn (II) by silver nanoparticles and AgNPs@SB is shown in **Figure 7 (a,b)** at adsorbent weight (0.005 gm) and p^H8, 6 and 4 respectively. **Table 4** and **Figure 7 (a, b)** shows the relation between the removal process of each metal ion and the equilibrium reaction time, for the adsorbent silver nanoparticles and AgNPs@SB respectively. The maximum adsorption was completed after 40 min. and then reached at equilibriumin the case of silver nanoparticles for all the metal ions. Instead for the AgNPs@SB, the maximum adsorption was completed after 20 min. and then reached at equilibrium for all the metal ions under examination.

3.2.4 Effect of adsorbent weight

The effect of adsorbent weight on metal ions Pb (II), Cd (II) and Zn (II) are investigated at different adsorbent mass from 0.001gm to 0.005 gm with constant parameter: initial metal ion concentration (5 to 15 ppm), contact time (20 min.) and p^H 8, 6 and 4 respectively is shown in **Figure 8 (a, b)**. The % removal of each metal ion was increased as the weight of adsorbent was increased and then reached at equilibrium. The maximum percentage removal of each metal ion obtained at 0.004 gm adsorbent weight in case of silver nanoparticles, instead for the AgNPs@SB the maximum percentage removal of each metal ion obtained at 0.002gm.

3.3 Adsorption isotherm

The efficiency of the adsorbent and the equilibrium relationship between adsorbate and adsorbent are described by the adsorption isotherm, which is defined as the ratio between the adsorbed and the remaining quantity in solution at equilibrium.

Langmuir and Freundlich isotherm described the oldest and easiest adsorption equation **[24]**.

The generalised form of Langmuir and Freundlich isothermwas represented by the following equation: -

(1) Langmuir

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max} C_e} + \frac{1}{q_{\max}}$$

Where, q_{max} = maximum adsorption capacity (mg g−1), q_e = amount of metal adsorbed per gram of the adsorbent at equilibrium, Ce = concentration of metal ion at equilibrium (mg L−1) K_L= Langmuir sorption constant (L mg−1) related to the free energy of sorption.

A plot of $1/qe$ versus $1/Ce$ produces a straight line with, intercept $1/q$max and gradient $1/KLq$max can be used to calculate $q$max are shown in **Figure 9 (a, b)**.

(2) Freundlich

$\log q_e = \log K_F + 1/n \log C_e$ (9)

Where, q_e = amount of metal adsorbed per gram of the adsorbent at equilibrium,

C_e = concentration of metal ion at equilibrium (mg L−1), K_F = Freundlich constant (L mg^{-1})

n = function of strength of adsorption obtained data from the Freundlich isotherm equation shown in **Figure 10 (a, b)**.

Based on obtained results, the adsorption capacity of of metal ions are in following order Zn > Pb > Cd. This order can be explainedon the basis of the ionic properties of metal ions such as ionic radii, electronic configuration and electro-negativity. It is known that, the surface complexation reaction is more influenced by the electrostatic attraction between the adsorbent and adsorbate. The electro-negativity and ionic radii of Pb (II) = (2.33, 1.20), Cd (II) = (1.69, 0.97) and Zn (II) = (1.65, 0.74) respectively. This means that the smaller the ionic radius and the higher electronegativity interact more strongly on the surface of adsorbent **[25-27]**.

Table 1: Physical properties of Schiff base and Ag nano@Schiff base

Compounds	Schiff base	Ag NPs@SB
Color	Orange-Yellow	Brick red colour
Yield	87.72%	91.39%
Melting point	120°C	150°C
Elemental analysis	C- 47.83%, H-41.30%, O-4.34%, N-6.50%	C-47.83%, H –41.30%, O – 4.34%, N – 6.50%
Molecular weight	357.42	465.28

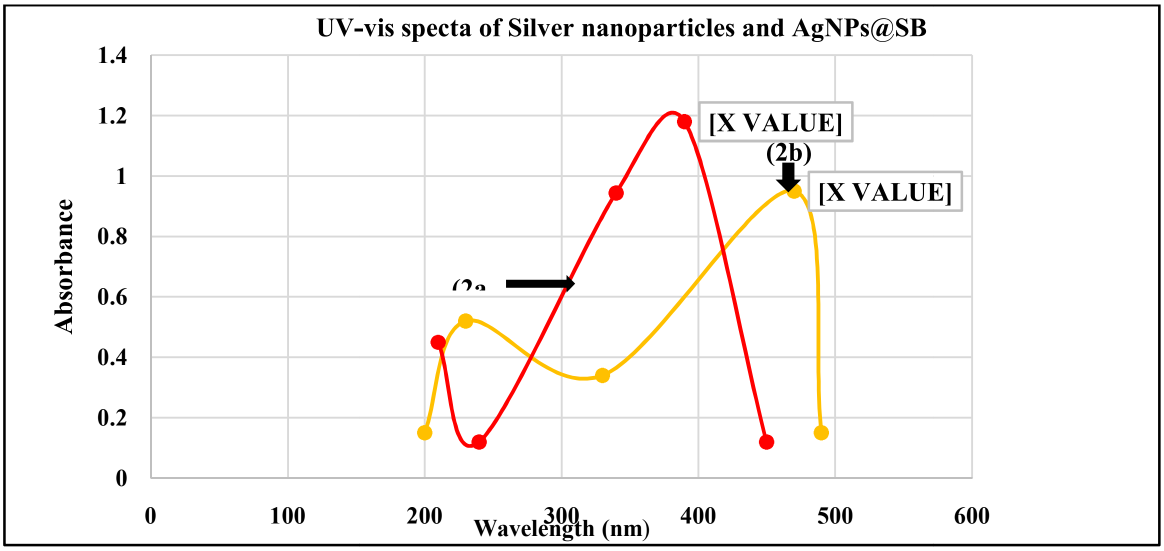

Figure (2a): UV-VIS spectra of silver nanoparticles and (2b) AgNPs@SB

Table 2: FTIR spectral studies of silver nanoparticles and Ag nano@Schiff base

Compound	υ(C=O) cm^{-1}	υ(C-N) aromatic cm^{-1}	υ (C=N) cm^{-1}	(Ag metal) cm^{-1}	υ (-OH) cm^{-1}	(N=O) cm^{-1}
Silver nanoparticles	_	_	_	572	3436	1637
AgNPs@SB	1750	1250	1650	572	3700	_

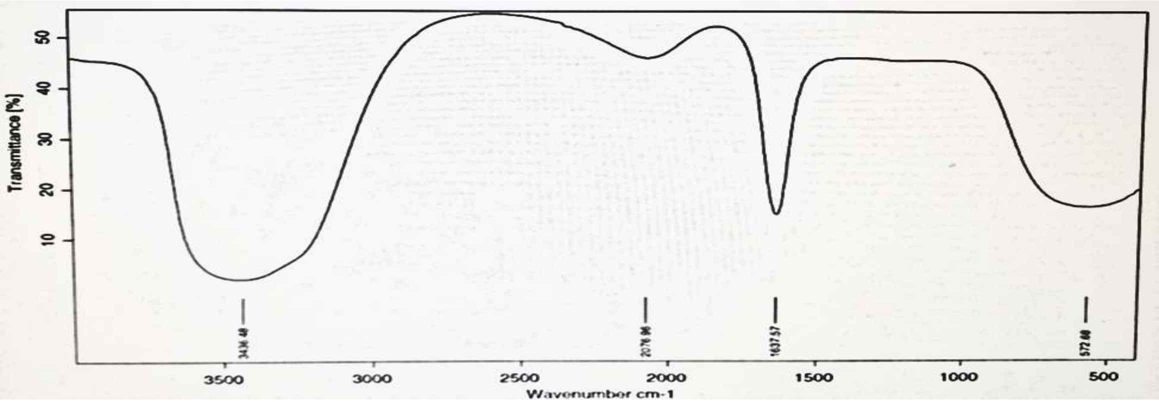

Figure 3a: FTIR spectra of silver nanoparticles

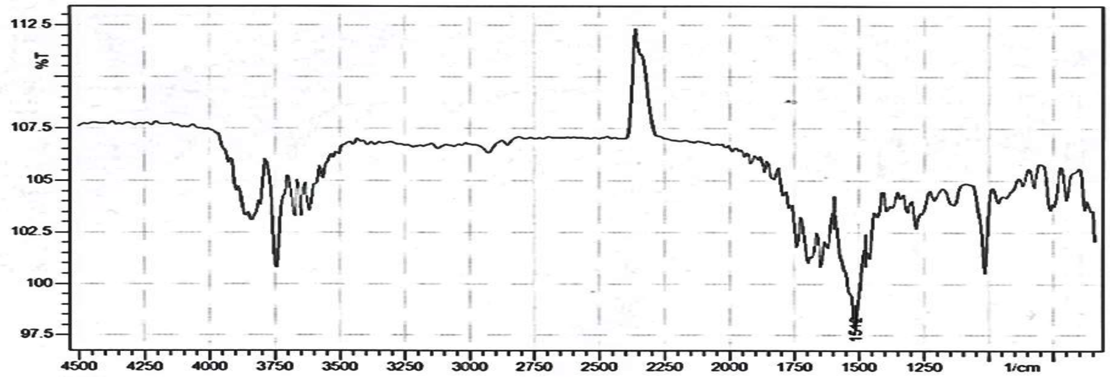

Figure 3b: FTIR spectra of AgNPs@SB

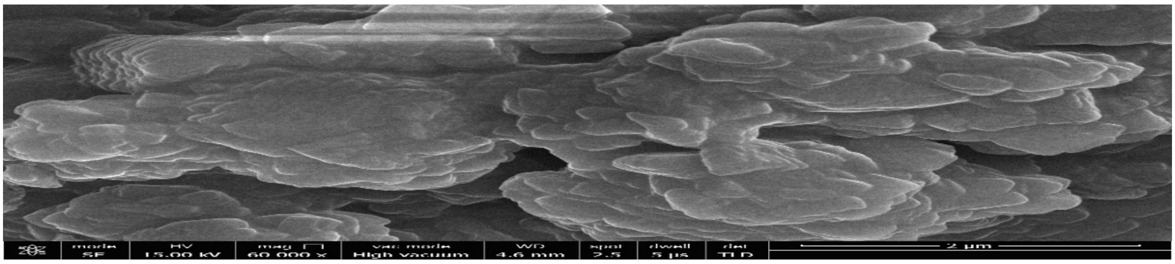

Figure 4a: SEM Image of silver nanoparticles

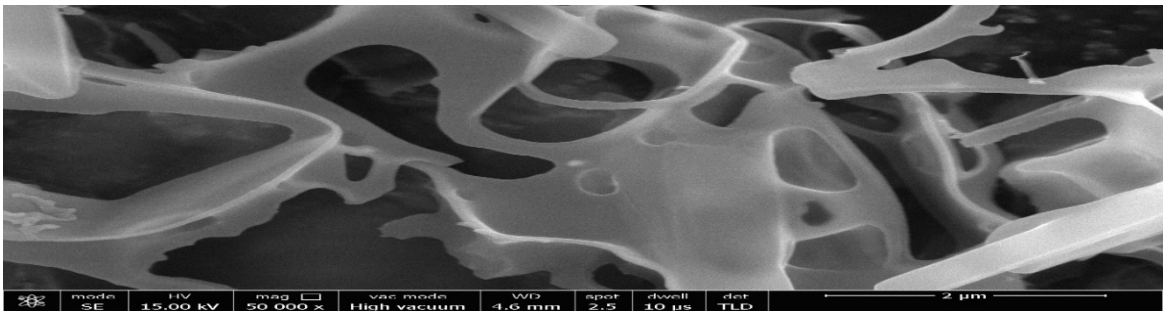

Figure 4b: SEM Image of silver nanoparticles

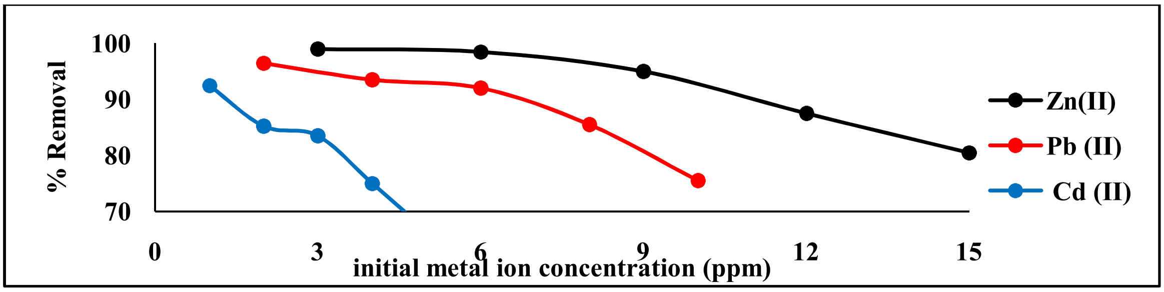

Figure 5 (a): Effect of initial metal ion concentration on % removal of Pb(II), Cd(II) and Zn(II) by AgNPs@SB

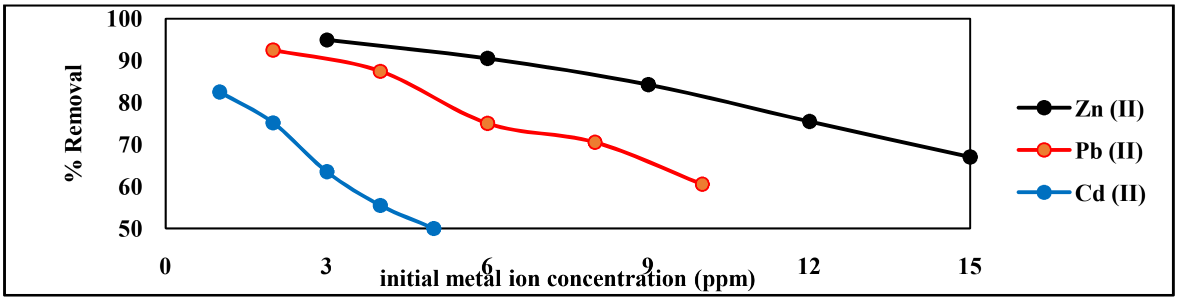

Figure 5(b): Effect of initial metal ion concentration on % removal of Pb(II), Cd(II) and Zn(II) by Silver nanoparticles

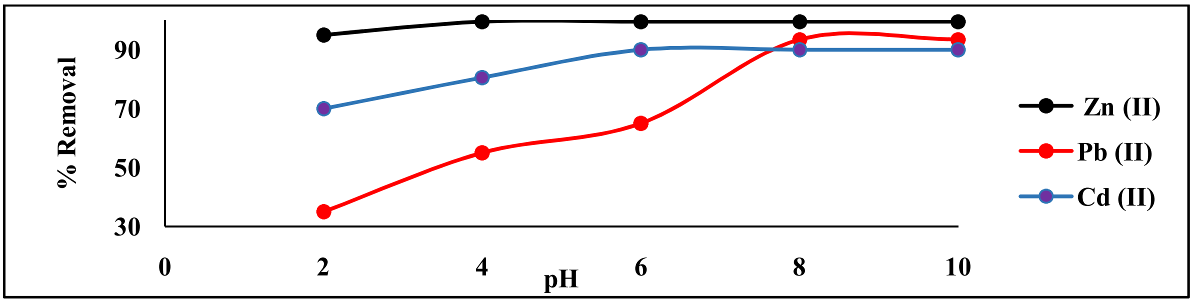

Figure 6(a): Effect of initial metal ion concentration on % removal of Pb(II), Cd(II) and Zn(II) by AgNPs@SB

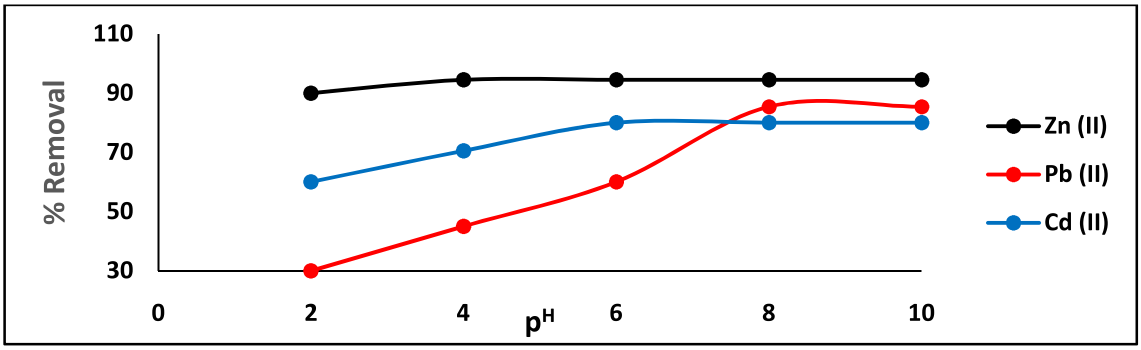

Figure 6 (b): Effect of initial metal ion concentration on % removal of Pb(II), Cd(II) and Zn(II) by Silver nanoparticles

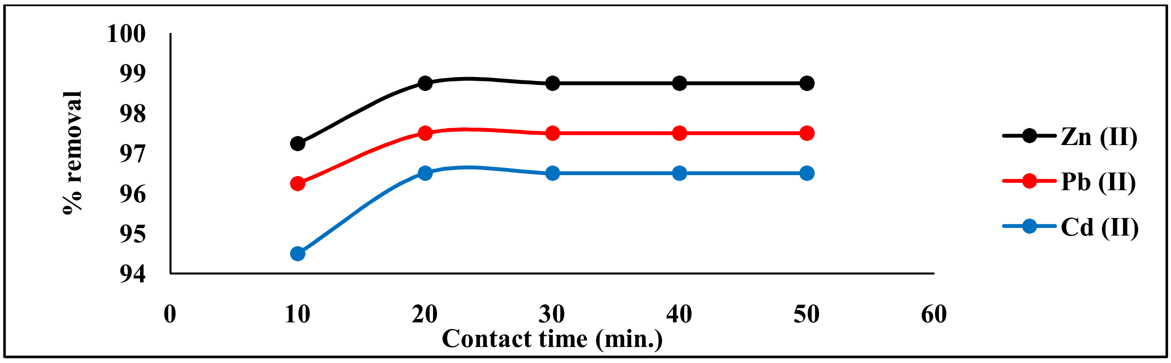

Figure 7 (a): Effect of contact time on % removal of Pb(II), Cd(II) and Zn(II) by AgNPs@SB

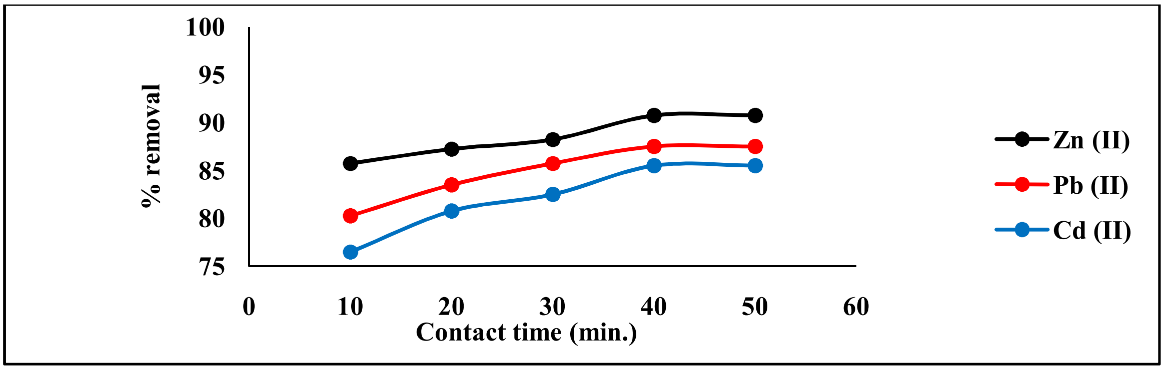

Figure 7 (b): Effect of contact time on % removal of Pb(II), Cd(II) and Zn(II) by Silver nanoparticles

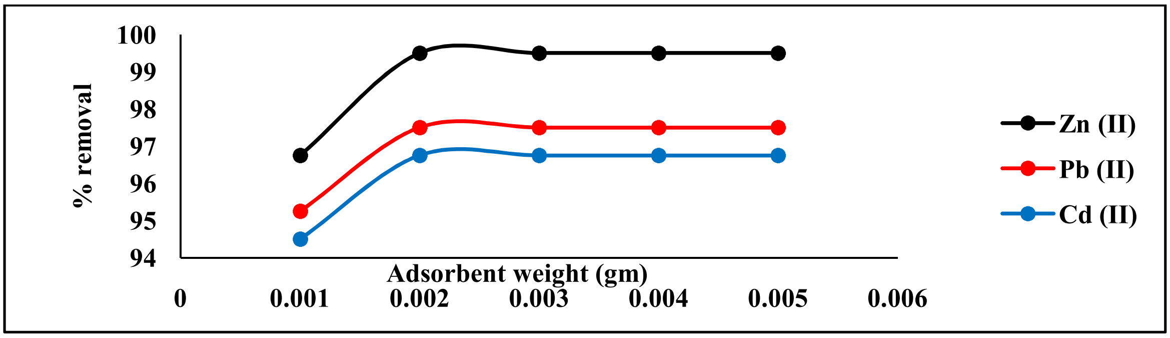

Figure 8(a): Effect of adsorbent weight on % removal of Pb(II), Cd(II) and Zn(II) by AgNPs@SB

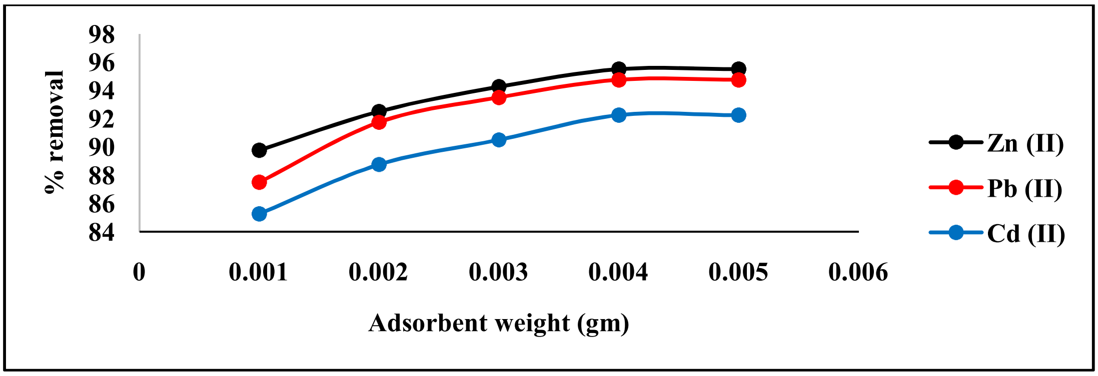

Figure 8 (b): Effect of contact time on % removal of Pb(II), Cd(II) and Zn(II) by Silver nanoparticles

Table 3: Parameters of Langmuir isotherm model for Pb (II), Cd (II) and Zn (II) on AgNPs@SB and Silver nanoparticles

Isotherm Model	Parameters	Pb (II)	Cd (II)	Zn (II)
Langmuir Model for AgNPs@SB	q_m	161.29	64.10	384.61
	K_L	0.258	0.305	0.161
	R^2	0.9983	0.9926	0.9933
Langmuir Model for Silver nanoparticles	q_m	64.10	61.34	99
	K_L	0.54	0.23	0.554
	R^2	0.9992	0.8497	0.9984

Table 4: Parameters of Frendulich isotherm model for Pb (II), Cd (II) and Zn (II) on AgNPs@SB and Silver nanoparticles

Isotherm Model	Parameters	Pb (II)	Cd (II)	Zn (II)
Frendulich ModelAgNPs@SB	K_F	29.75	14.93	48.26
	1/n	0.377	0.432	0.284
	R^2	0.9128	0.9665	0.9284
Fendulich ModelSilver nanoparticles	K_F	19.47	10.96	30.54
	1/n	0.367	0.456	0.365
	R^2	0.9843	0.5713	0.971

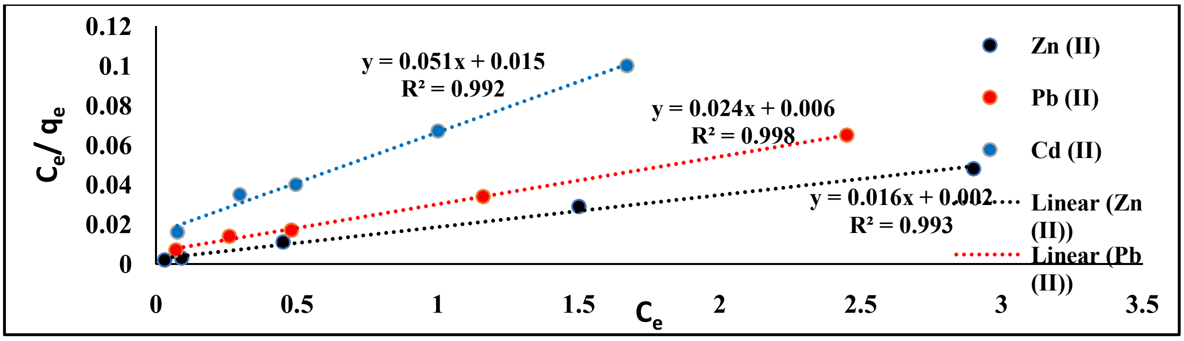

Figure 9 (a): Effect of Langmuir isotherm on Pb(II), Cd(II) and Zn(II) by AgNPs@SB

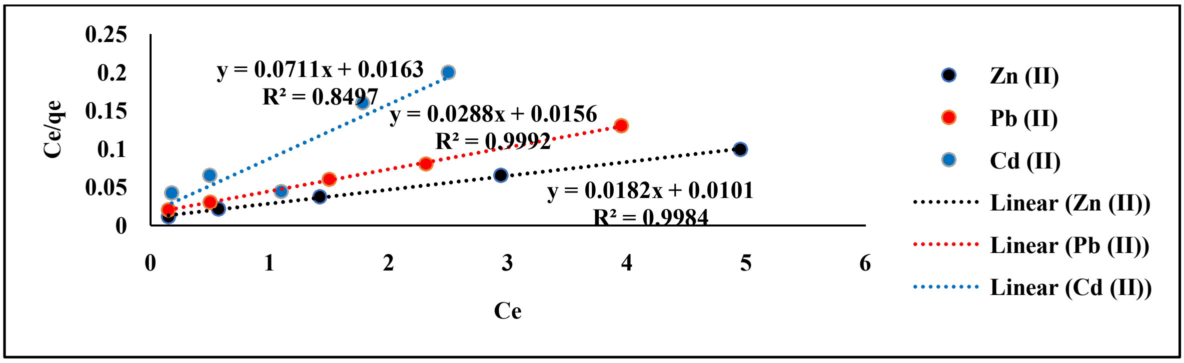

Figure 9(b): Effect of Langmuir isotherm on Pb(II), Cd(II) and Zn(II) by Silver nanoparticles

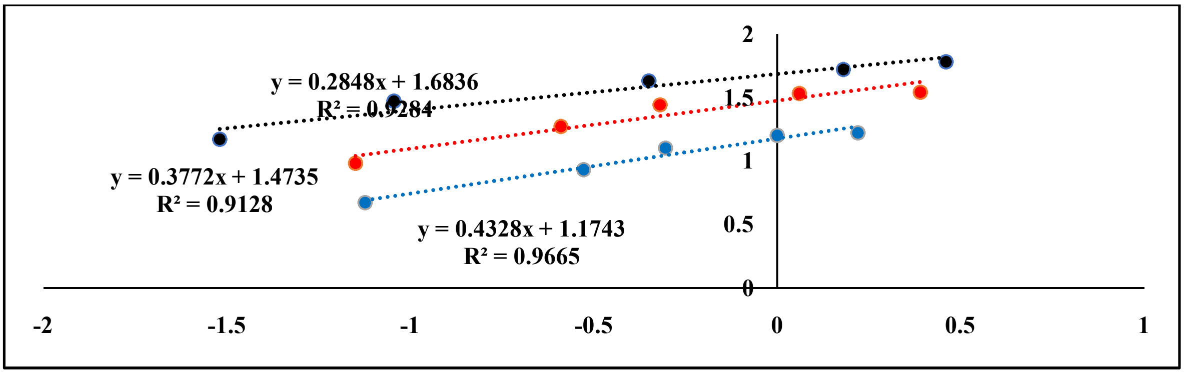

Figure 10(a): Effect of Freundlich isotherm on Pb(II), Cd(II) and Zn(II) by AgNPs@SB

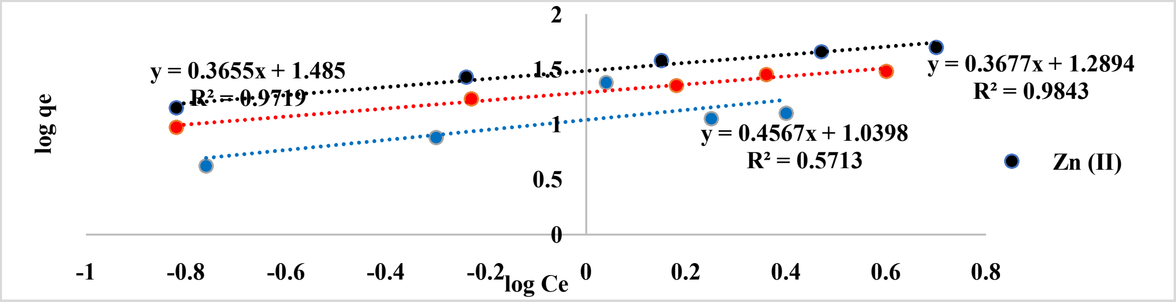

Figure 10(b): Effect of Freundlich isotherm on Pb(II), Cd(II) and Zn(II) by Silver nanopartcles

5. CONCLUSION

Modified silver nanoparticles with Schiff base are able to be used as effective adsorbent for removal of lead, cadmium and zinc metal ions from industrial waste with respect to unmodified silver nanoparticles. The experimental results indicate that the equilibrium time required for a maximum adsorption for Pb (II), Cd (II) and Zn (II) on AgNPs@SB and Silver nanopartices is 20 min. and 40 min. respectively. The maximum adsorption capacity for Pb (II) = 161.29, Cd (II) = 64.10 and Zn (II) = 384.61 respectively, for AgNPs@SB and Pb (II) = 64.10, Cd (II) = 61.34 and Zn (II) = 99 respectively for silver nanoparticles. The obtained results of adsorption isotherm studies indicate that Langmuir isotherm model is the most fit model to describe and evaluate the adsorption process for each metal ion then Freundlich isotherm model.

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REFERENCES

[1] Shah B. A., Shah A. V., Shah P. M., Analytical and Morphology Studies of Phthalic acid Formaldehyde Resorcinol as Chelating Resin, Malaysian Polymer Journal (MPJ), 4 (2), 2009, 112.

[2] Cavaco S. A., Fernandes S., Augusto C. M., Quina M. J., Gando-Ferreira L. M., Evaluation of chelating ion – exchange resin for separating Cr (III) from Industrial effluents, j. of Hazard. Mater, 169, 2009, 516-523.

[3] Quality Directive of Potable Water, Second ed., WHO (World Health Organization).

[4] Chiban M., Soudani A., Sinan F., Persin M., Single, binary and multi-component adsorption of some anions and heavy metals on environmentally friendly Carpo-brotus edulis plant, Colloids Surf., B, 82, 2011, 267-276.

[5] Kyzas G. Z., Kostoglou M., Lazaridis N. K., Lambropoulou D. A., Bikiaris D. N., Environmental friendly technology for the removal of pharmaceutical contaminants from wastewaters using modified chitosan adsorbents, Chem. Eng. J., 222, 2013, 248-258.

[6] Gupta V. K., Ganjali M. R., Nayak A., Bhushan B., Agarwal S., Enhanced heavy metals removal and recovery by mesoporous adsorbent prepared from waste rubber tire, Chem. Eng. J., 197, 2012, 330-342.

[7] Ciesielczyk F., Bartczak P., Wieszczycka K., Siwinska-Stefanska K., Nowacka M., Jesionowski T., Adsorption of Ni (II) from model solution using co-precipitated inorganic oxides, Adsorption, 19, 2013, 423-434.

[8] Rudnicki P., Hubicki Z., Kilodynska D., Evaluation of heavy metal ions removal from acidic waste water streams, Chem. Eng. J., 252, 2014, 362-373.

[9] Kolodynska D., Kowalczyk M., Hubocki Z., Evaluation of iron-based hybrid materials for heavy metal ions removal, Mater. Sci., 49, 2014, 2483-2495.

[10] Janschm M, Stumf P, Graf C, Ru ¨hi E, Mu ¨ller RH, Adsorption kinetics of plasma proteins on ultrasmall superparamagnetic iron oxide (USPIO) nanoparticles, Int J Pharm, 428, 2012, 125–133.

[11] Yu J-G, Zhao X-H, Yang H, Chen X-H, Yang Q, Yu L-Y, Jiang J-H, Chen X-Q, Aqueous adsorption and removal of organic contaminants by carbon nanotubes, Sci Total Environ, 482–483, 2014, 241–251.

[12] O ¨nnby L, Svensson C, Mbundi L, Busquets R, Cundy A, Kirsebom H , c-Al2O3-based nanocomposite adsorbents for arsenic(V) removal: assessing performance, toxicity and particle leakage. Sci Total Environ, 473–474, 2014, 207–214.

[13] Turker AR AR., New Sorbent for Solid-Phase Extraction for Metal

Enrichment, Clean-Soil, Air, Water, 35(6), 2007, 548-57.

[14] Gaikwad V. K., Yadav U. M., Metal complexes of schiff bases, Sch. Res. J. Interdiscip. Stud., 3, 2016, 2225–2234.

[15] Shakdofa M. M.,Shtaiwi M. H., Morsy N., Abdel-rassel T., Metal complexes of hydrazones and their biological, analytical and catalytic applications: a review, Main Group Chem., 13, 2014, 187–218.

[16] Nworie F. S., Nwabue F. I., Elom N. I., Eluu S. O>, Schiff bases and Schiff base metal complexes: from syntheses to applications, J. Basic App. Res., 2, 2016,295–305.

[17] Bader N. R., Applications of Schiff's bases chelates in quantitative analysis-A review, Rasayan J. Chem., 3, 2010, 660–670.

[18] Harvey D., Clifford C., Bis (N, N-1-Disalicylethlene Diamine Metthoxyphenylmethylidene), M 5321 Journal of Open Access Publication Mol. Bank, 352, 2004.

[19] Dogan S., Dinçer Kaya F. N., Atakol O., Enrichment of copper and nickel with solid phase extraction using multiwalled carbon nanotubes modified with Schiff bases, Int. J. Environ. Anal. Chem., 95, 2015, 698–712.

[20] Khan M., Yilmaz E.,Soylak M., Vortex assisted magnetic solid phase extraction of lead(II) and cobalt(II) on silica coated magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)-2-naphthol, J. Mol. Liq., 224, 2016, 639–647.

[21] Banee V. Shivaji, Patil M. S., Kulkarni R. M., Patil S.J., Synthesis and Characterization of Silver Nano Particles for EDM Applications, Materials Today: Proceedings, 4, 2017, 12054-12060.

[22] Elias Elemike Emeka, EnockDare Olugbenga, Inyang Samuel David, Jude, Onwuka Chinedu, 2-Imino-(3,4-dimethoxybenzyl) ethane sulfonic acid Schiff bae anchored silver nanocomplex mediated by sugarcane juice and their antibacterial activities, J. of Applied Research and Technology, 14,2016, 38-46.

[23] Magda A AKL, Abdel M Fatah, Assad H Hassan, Heba Maher, Synthesis, Characterization and Evaluation of Peanut Shells-Derived Activated Carbons for Removal of Methomyl from Aqueous solutions, J. Environ Anal Toxicol, 6 (2), 2016, 1000352.

[24] Jalali R., Ghafourian H., Asef Y., Davarpanah S. J., Sepehr S., Journal of Hazardous Materials, 92 (3), 2002, 253-262.

[25] Uzum I., Guzel F., Turk J. Chem., 24, 2000, 291-29.

[26] Sonmezay A., Oncel M.S., Bektas N., Adsorption of lead and cadmium ions from aqueous solutions using manganoxide minerals, Trans. Nonferrous Met. Soc. China, 22, 2012, 3131-3313.

[27] Mousa S. M., Amar N. S., Ibrahim H. A., Removal of lead ions using hydroxylapatite nano-material prepared from phosphogypsum waste, J. Saudi Chem. Soc., 20 (3), 2016, 357-365.