



Schiff Base Anchored with Silver Nanoparticles as Effective Adsorbent for Removal of Cadmium(II) Heavy Metal from Industrial Wastewater

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The current study deals with the examination of the capacity of Schiff base anchored with silver nanoparticles for removal of cadmium(II) ions from industrial wastewater. Schiff base was synthesized using refluxing of salicylaldehyde and 4-aminoantipyrine in alcoholic medium. The characterization of Schiff base were studied by elemental analysis, FTIR, NMR, UV-visible and mass spectral studies. The silver nanoparticles were synthesized using the chemical reduction method and characterized. Then, silver nanoparticles anchored to the Schiff base by suitable method and again characterized. Peanut shells were used as solid phase for removal of Cd(II) ions. The effects of several parameters to optimize the adsorption of Cd(II) ions on solid phase, including pH, contact time, initial metal ion concentration and adsorbent weight were investigated. The maximum removal efficiency of Cd(II) ions on solid phase using Ag nano@Schiff base was achieved under experimental conditions of pH 6 (% removal = 81%), contact time of 15 min (% removal = 93%), initial metal ion concentration of 0.5 ppm (% removal = 95%) and adsorbent weight of 3 mg (% removal = 89%). The results showed that extraction of Cd²⁺ on AgNPs@Schiff base follows Freundlich adsorption isotherm.

Keywords: Heavy metal, Schiff base, Adsorption, Silver nanoparticles.

INTRODUCTION

Today, one of the major ecological concerns on a world scale is heavy metal pollution from both anthropogenic and natural sources and increasing day by day [1]. However, the majority of this heavy metal pollution is related to anthropogenic activities such as smelting, mining, industrial wastes, untreated urban sewage sludge discharge and many other human activities [2]. Such high levels of toxic heavy metals have an adverse effect on the mankind [3]. Many procedures are used to eliminate several toxic heavy metals from wastewaters before discharging it into the mother nature which includes membrane filtration, chemical precipitation, electrochemical process, ion exchange, super critical fluid extraction, membrane bioreactors, advanced oxidation process and adsorption [4]. Now a days, for heavy metal extraction, adsorption technique has evolved as an effective and economic method [5-7].

Schiff base is synthesized when any primary amine reacts with an aldehyde or ketone under specific condition. Structurally, a Schiff base (also known as imine or azomethine) is

a nitrogen analogue of an aldehyde or ketone in which the carbonyl group has been replaced by an imine or azomethine group. Schiff base ligands are easily synthesized and form complexes with metal ions. Over the last few years, many reports have come to their biological applications, including antibacterial [8], antiviral activity [9], anticancer [10], antimalarial [11], antifungal [12] and anti-inflammatory [13]. One of the Schiff base ligand characteristics is that its ability in water treatment process is currently under study [14,15]. However, these materials have a relatively low adsorption efficiency [16]. Hence, it is necessary to find more effective adsorbents, which could be highly selective, cost-effective and environment friendly [17-19].

Several studies have been reportedly recently that these requirements can be achieved by using nanomaterials [20-23]. It was also reported that the nanomaterials such as graphene, zinc oxide, titanium oxide, magnesium oxide, ferric oxide, manganese oxide and carbon nanotubes (CNTs) played a vital role in the wastewater treatment processes [24-32]. Among inorganic nanoparticles, silver nanoparticles (AgNPs) have

attracted many researchers' attention due to their physical, chemical and biological prop-erties as compared to their bulk form [33,34]. The aim of this study is to evaluate the maximum capacity of a silver nano complex of Schiff base synthesized by suitable method to remove cadmium(II) ions from industrial wastewaters. The continuous adsorption process has been used to evaluate the maximum adsorption capacity of a silver nano complex of Schiff base.

EXPERIMENTAL

4-Aminoantipyryne, salicylaldehyde and sodium borohydride were purchased from CDH Chemicals, India. Methanol, ethanol, sodium citrate dihydrate and silver nitrate were purchased from Sigma-Aldrich, USA. All the solvents were distilled dried and purified by standard methods.

Synthesis of Schiff base: A solution of salicylaldehyde in ethanol mixed with a solution of 4-aminoantipyryne in ethanol and stirred for 10 min and then refluxed for 2-3 h. The yellow coloured precipitate was filtered and recrystallized from alcohol to remove the impurities (**Scheme-I**). The purity of the ligand was confirmed by TLC technique. Colour: yellow; yield: 81.72%. m.w.: 307.36; m.p.: 184 °C. Elemental analysis found %: C, 70.27; H, 5.53; O, 10.41 and N, 13.66.

Synthesis of silver nanoparticles: Established volume of trisodium citrate dihydrate solution mixed with a fixed volume of silver nitrate solution and this reaction mixture was added dropwise to ice cooled sodium borohydride solution. The reaction mixture was stirred vigorously on magnetic stirrer for 10 min. After 10 min, the stirring was stopped and a yellow colloidal solution of silver nanoparticles was obtained.

Synthesis of Ag nano@Schiff base: Synthesis of silver nanocomplex of Schiff base was done by binding the synthesized Schiff base on the synthesized colloidal silver nanoparticles solution. To the silver nanoparticles colloidal solution, salicylaldehyde solution and 4-aminoantipyryne solutions were added and stirred for 10-15 min obtaining a bright light green coloured precipitate. Yield: 82.39%. m.w.: 415.22; m.p.: 176 °C. Elemental analysis found %: C, 52.02; H, 4.09; O, 7.70; N, 10.11 and Ag, 25.97.

Synthesis of solid phase: Peanut shells were used as a solid phase in the adsorption process. Peanut shells were first washed with 0.5% HCl to remove all dirt, dried in oven for overnight, grounded by a mill, sieved and carbonized for 2 h. The carbonized material was soaked in NaOH for overnight, then dehydrated in an oven for overnight and activated for 2 h. The resulting activated carbon was washed with distilled water, filtered and finally dried in an oven.

Extraction of cadmium(II): A silver nanocomplex of Schiff base was attached with solid phase. About 2 mg of solid phase was added to a silver nanocomplex of Schiff base dissolved in 10 mL of ethanol. The obtained precipitate was dried in oven at 60 °C for 5 h. [35]. Then, the metal ions were extracted from industrial wastewater by continuous adsorption method.

A glass column is used in column method, where activated carbon was put between two layers of glass wool, the first at the bottom and second at the top to retain it. Then, water sample containing silver nanocomplex of Schiff base passed through the column at the flow rate 2.0 mL/ min.

The percentage removal of metal ion was calculated as follows:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where, C_o is the initial concentration of metal ion and C_e is the concentration of metal ion at equilibrium.

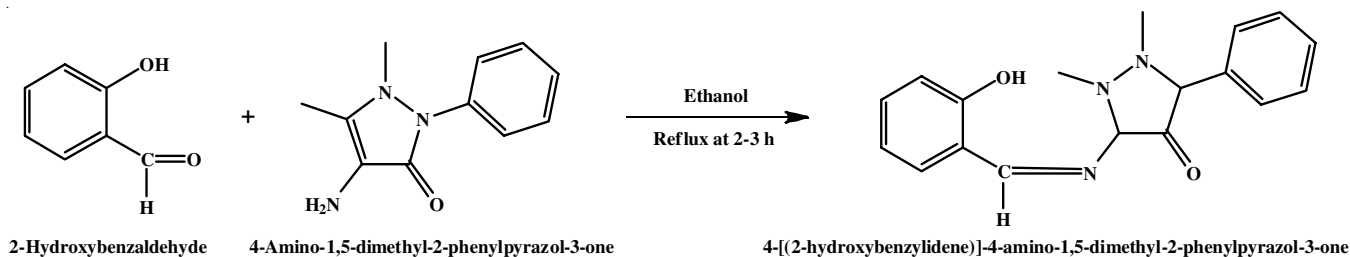
RESULTS AND DISCUSSION

UV-visible spectral studies: In Fig. 1a, four bands are observed in DMSO medium. Bands A and B appeared at 220 and 250 nm, respectively due to $\pi-\pi^*$ transition in aromatic ring. Band C appeared at 350 nm due to $n-\pi^*$ transition in between (CH=N-) bond, while band D appeared at 400 nm wavelength due to intramolecular H-bonding between the hydroxyl group of salicylaldehyde and azomethine nitrogen.

In silver nanoparticles formation, it was observed that colour of silver nitrate solution turned colourless to yellow, which indicates the formation of colloidal silver nanoparticles due to plasmon absorbance and showed surface plasmon resonance (SPR) peak at 415 nm (Fig. 1b). Previous studies [36] suggested that an SPR peak located between 410 and 450 nm has been observed for AgNPs and might be attributed to spherical nanoparticles.

In the UV-visible spectra of Ag nano@Schiff base (Fig. 1c), an absorption band is observed at 460 nm thus, the spectrum shows shifting of absorption band at higher wavelength which confirms the formation of Ag nano@Schiff base. The other absorption bands at 220, 250 and 350 nm were similar as in synthesized Schiff base and silver nanoparticles.

FTIR spectral studies: In the FTIR spectrum of Schiff base (Fig. 2a), a strong band appeared at 1589 cm^{-1} is due to $\nu(\text{C}=\text{N})$. The bands appeared at 3055 and 1281 cm^{-1} , respectively, due to the C-H aromatic stretching and -OH bend vibration, respectively. In the IR spectrum of Ag nano@Schiff base (Fig. 2b), $\nu(\text{C}=\text{N})$ peak is observed at 1589 cm^{-1} . The peaks at 3750 ,



Scheme-I: Synthesis of Schiff base

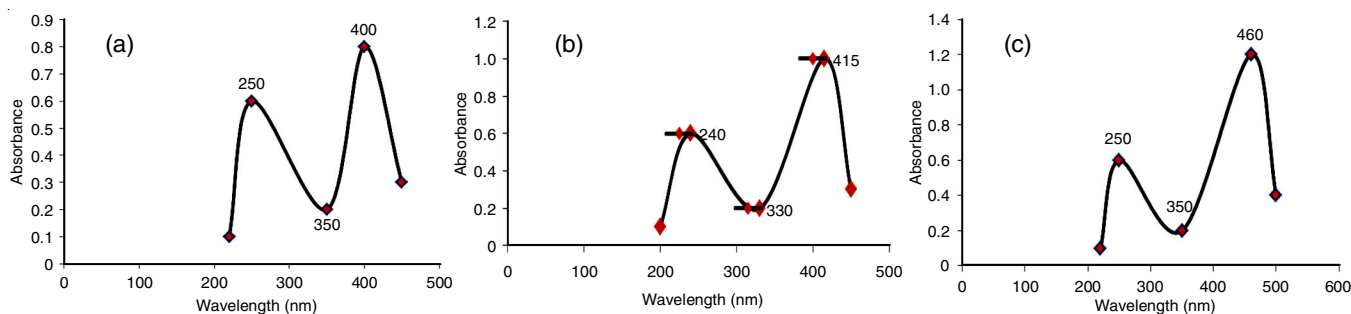


Fig. 1. UV-vis spectra of Schiff base (a); silver nanoparticle (b); and Ag nano@Schiff base (c)

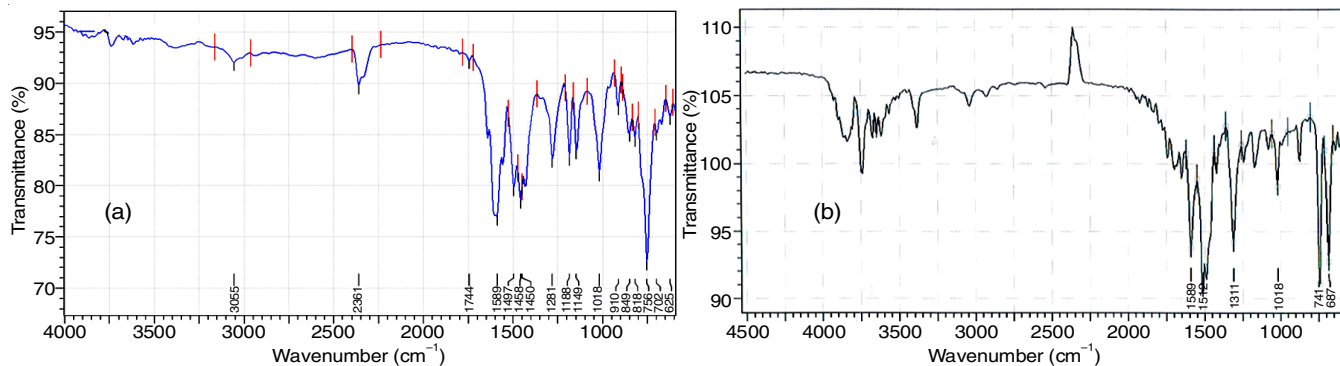


Fig. 2. FTIR spectra of Schiff base (a); and Ag nano@Schiff base (b)

3300 and 3050 cm⁻¹ are observed due to the -OH, -CH aromatic and -CH aliphatic, respectively. An appearance of new strong absorption band is also observed at 687 cm⁻¹ which indicates the formation of Ag nano@Schiff base.

Mass spectral studies: The mass spectrum of Schiff base (Fig. 3a) showed a peak at m/z 308.02 due to $M^+ + 1$. This is equivalent to the molecular weight of the proposed structure. In the mass spectrum of Ag nano@Schiff base (Fig. 3b), a peak observed at m/z 403.07 is due to coating of silver nanoparticles on Schiff base. Molecular weight of Ag nano@Schiff base was almost 415.22 because of addition of silver. Thus, the molecular ion peak was shifted from 307.36 to 415.22, which indicate the coating of silver nanoparticle on Schiff base.

NMR studies: The ¹H NMR spectrum of Schiff base shows singlet for azomethine proton at 9.8 ppm, multiplet for C₆H₅

at 6.8-7.5 ppm, singlet for =C-CH₃ at 2.4 ppm and singlet for N-CH₃ at 3.1 ppm (Fig. 4).

SEM studies: Fig. 5a shows that the synthesized silver nanoparticles have particle size 30-40 nm confirms the nanostructure of silver nanoparticles, while Fig. 5b, indicates the floral structure of Ag nano@Schiff base, which is suitable for adsorption studies.

Effect of pH: From Fig. 6, it is observed that the rate of removal of Cd(II) increases rapidly, from 29% to 81% as pH increased from 1 to 6 and then become constant when increases the pH value from 7 to 8. At the lower pH value (<6), cadmium is presented in form of Cd²⁺ ions. Therefore, the lower adsorption percentage of Cd²⁺ on silver nanocomplex of Schiff base at lower pH values partly depends on the electrostatic repulsion occurring between H⁺ and Cd²⁺ on the silver nanocomplex of

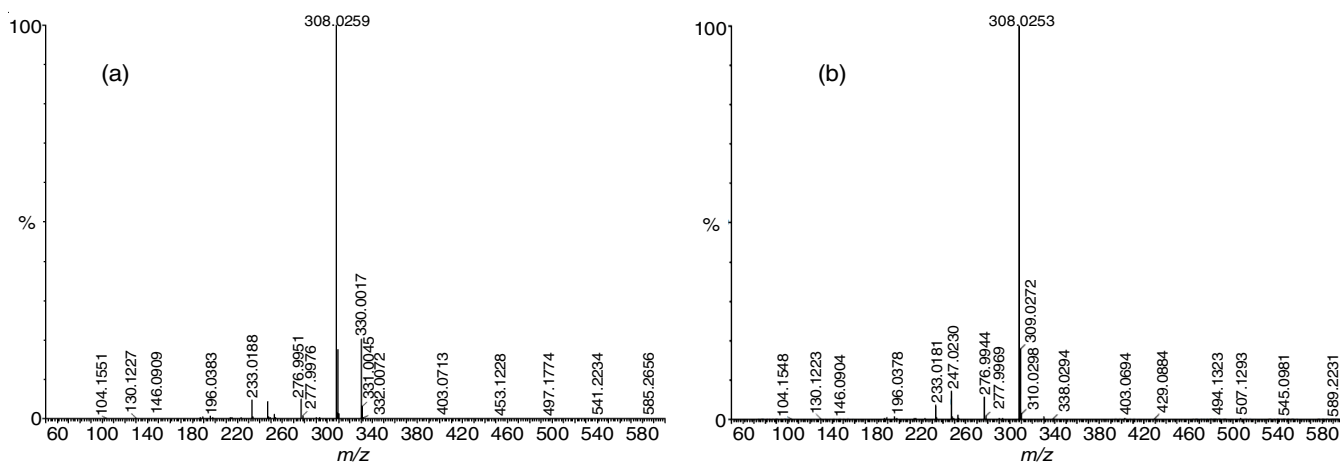


Fig. 3. Mass spectra of Schiff base (a); and Ag nano@Schiff base (b)

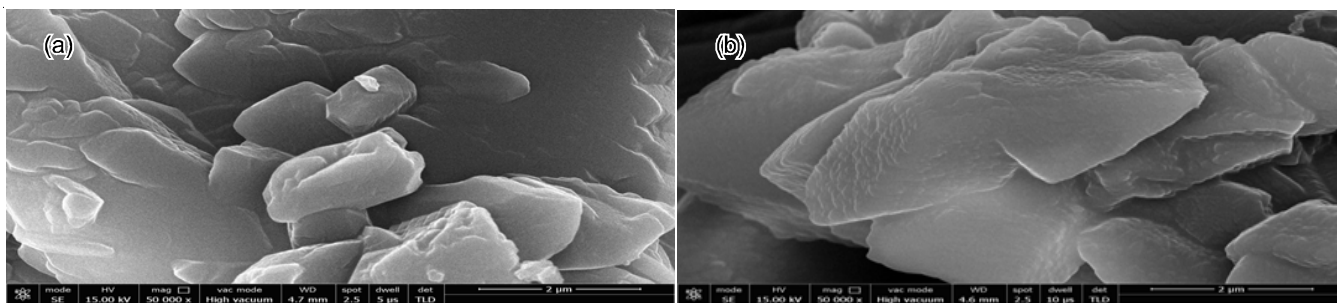


Fig. 5. SEM image of silver nanoparticle (a); and Ag nano@Schiff base (b)

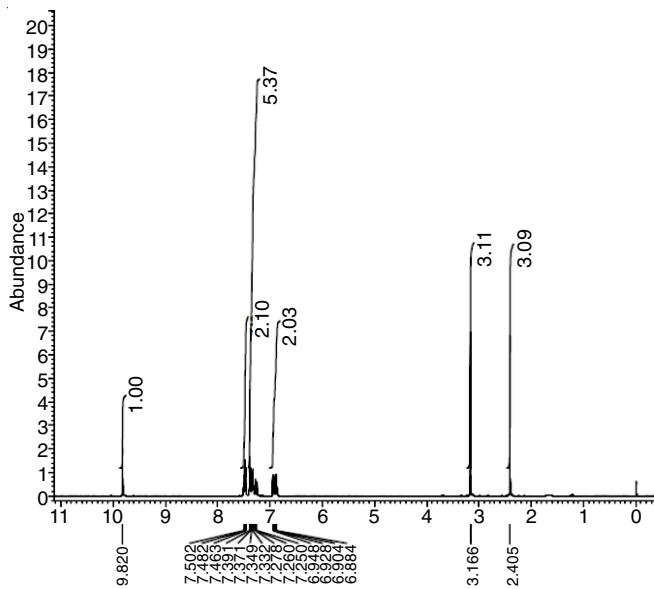


Fig. 4. ¹H NMR spectra of Schiff base

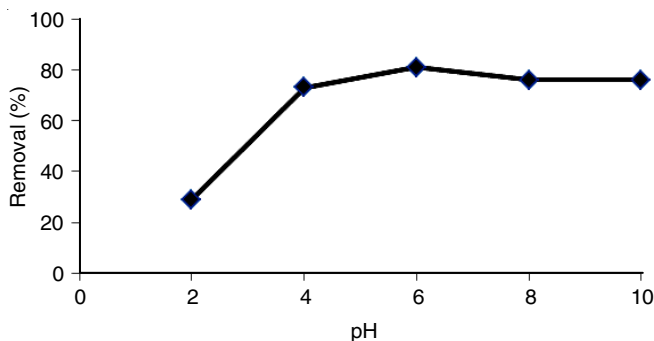


Fig. 6. Effect of pH on removal (%) of Cd²⁺ by silver nanocomplex of Schiff base

Schiff base. The removal rate of Cd²⁺ ion is maximum at pH value 6 due to the precipitation of cadmium as Cd(OH)₂. Thus, pH 6 is the most optimum value for this chelation.

Effect of Cd²⁺ concentration: Fig. 7 shows the effect of initial metal ion concentration on percentage removal of Cd²⁺ ions by a silver nanocomplex of the Schiff base from a water sample. It is observed that increasing the initial concentrations of Cd²⁺ decreases the removal capacity. Maximum removal of Cd²⁺ takes place at concentration of 0.5 ppm of Cd²⁺ metal ion in water sample. The reason is attributed due to the saturation of all binding sites with metal ions and establishment of equilibrium between adsorbate and adsorbent [37,38].

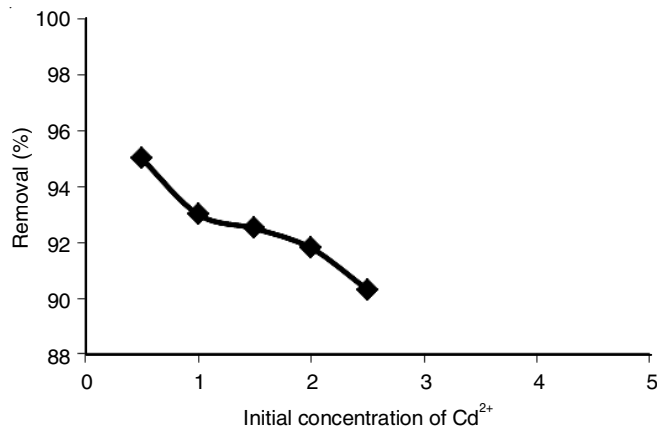


Fig. 7. Effect of initial concentration on removal (%) of Cd²⁺ by silver nanocomplex of Schiff base

Effect of contact time: Fig. 8 shows the effects of contact time on the percentage removal of Cd²⁺ ions by silver nanocomplex from a water sample at the optimized conditions. The maximum adsorption achieved after 15 min of adsorption at pH 6 and then reached at equilibrium. Thus, 15 min is considered as the optimum contact time for Cd²⁺ adsorption on silver nano complex of Schiff base.

Effect of adsorbent weight: Fig. 9 shows the effects of different amount of adsorbent weight on percentage removal of Cd²⁺ ions by a silver nanocomplex of Schiff base from a water sample at constant initial metal ion concentration, pH,

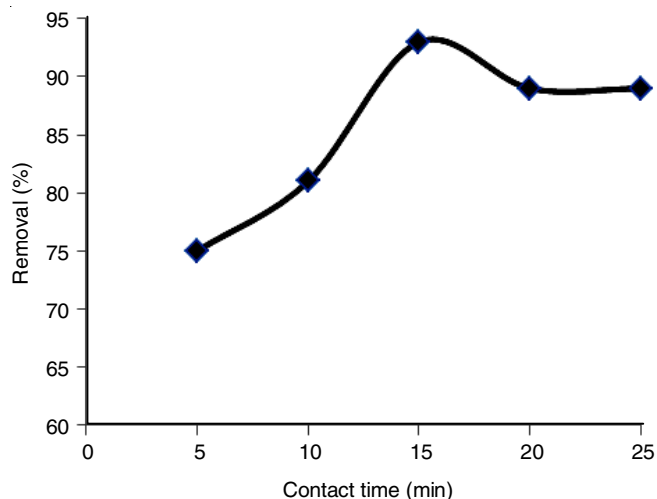


Fig. 8. Effect of contact time on removal (%) of Cd²⁺ by silver nanocomplex of Schiff base

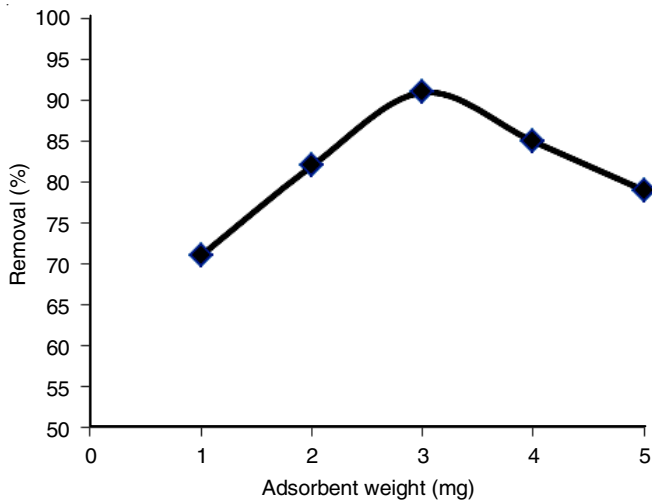
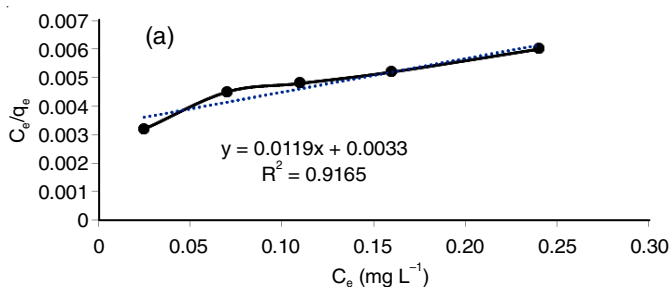


Fig. 9. Effect of adsorbent weight (mg) on the removal (%) of Cd²⁺ by silver nanocomplex of Schiff base

and contact time. The percentage of adsorbed cadmium increased as the weight of adsorbent was increased from 1 to 3 mg and then, followed by a decrease of percentage removal of Cd²⁺ as adsorbent weight increased.

Adsorption isotherm: The relation of equilibrium data is essential to apply Langmuir [39] and Freundlich [40] isotherms in order to analysis the experimental data of the AgNPs@Schiff base adsorbent for Cd (II) ions. For the evaluation of adsorption equilibrium curve of Cd(II), added 3 mg of AgNPs@schiff base (adsorbent) in 50 mL wastewater sample with various concentrations of Cd(II) at pH 6.

The equilibrium adsorption capacity (q_e) is calculated by following equation:



$$q_e = \frac{C_o - C_e}{m \times V} \quad (2)$$

Here, C_o and C_e are the initial and final concentration of Cd(II) in the wastewater sample (mg L^{-1}), q_e is the amount of adsorbed Cd(II), V is the volume (L) of wastewater sample and m is the composite mass (g).

In this study, Langmuir and Freundlich models demonstrated for Cd(II) on AgNPs@Schiff base are shown in Figs. 10a-b.

The general linearized form of Langmuir is as follows:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m K_L} \right) + \frac{C_e}{q_m} \quad (3)$$

The general linearized form of Freundlich isotherm is as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where, C_e is the final concentration of Cd(II) in the wastewater sample (mg L^{-1}), q_e is the equilibrium adsorption capacity (mg mg^{-1}), and K_L and K_F are the equilibrium constant (L mg^{-1}) and q_m is the maximum amount of Cd(II) per unit mass of adsorbent. Obtained parameters from the graph are given in Table-1.

From the above outcomes the synthesized adsorbent silver nanocomplex of Schiff base equilibrium capacity approved. The maximum adsorption capacity obtained in this work is compared to other adsorbents indicates the better efficiency of the synthetic adsorbent (Table-2).

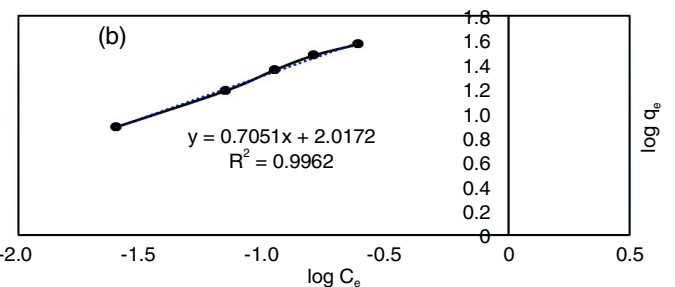


Fig. 10. Langmuir (a) and Freundlich (b) adsorption isotherms for Cd²⁺ on silver nanocomplex of Schiff base

Langmuir: $C_e/q_e = (1/q_m K_L) / C_e + 1/q_m$			Freundlich: $\log q_e = \log K_F + 1/n \log C_e$		
q_m (mg g^{-1})	K_L (L g^{-1})	R^2	K_F (L g^{-1})	R^2	$1/n$
84.38	3.58	0.9165	104.7	0.9962	0.705

Adsorbents	q_{\max} (mg g^{-1})	Ref.
Chromium doped NiO nanoparticles	0.1119	[41]
Zero valent silver nanoparticle	0.845	[42]
Cd(II) Imprinted silica supported hybrid sorbent with an anchored Schiff base	31.4	[43]
Sol-gel derived MgO-SiO ₂	94.05	[44]
AgNPs@Schiff base	84.38	This study

Conclusion

In this work, a Schiff base anchored silver nanocomplex attached with solid phase (activated carbon) has been used as novel adsorbent for the removal of cadmium ions effectively. The results showed that the maximum removal capacity of Cd²⁺ ions by Ag nano@Schiff base is obtained under the optimized conditions of pH 6 (% removal = 81%), initial metal ion concentration of 0.5 ppm (% removal = 95%), contact time of 15 min (% removal = 93%) and adsorbent weight of 3 mg (% removal = 89%). The removal of cadmium ions from industrial wastewater is achieved due to the high surface area and low particle size, which provides maximum adsorption active sites. In addition, it was seen that Freundlich isotherm has a better value of correlation coefficient (R²) of 0.9962 with the experimental findings rather than with Langmuir isotherm. The adsorption mechanism of AgNPs@Schiff base is defined by both chelating and ion exchange.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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