Removing some heavy elements from their chemical solutions by benzimidazole azo reagent

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Abstract

In this articl, we synthezed an azo- benzimidazole reagent to remove the lead and cadmium ions from therir solutions. The yeled of the reagent was high reching 80%. The infrared spectroscopy refres to exit important groups such as hydroxy, N-H, C=N, C=C and azo group which give the color for the regeant. The X-RD spectroscopy indicates crystaline nature of the azo- benzimidazole reagent. The azo- benzimidazole reagent exhibted amisaing ability to remove the cadmium ions in large range of the concentrations and at low concentrations of lead ions with high sensetivity.

1. Introduction

Heavy metals are toxic in general and non-biodegradable. They come to the environment mainly through industrial, mining and agricultural activities (1). Industrial wastewaters are heavily loaded with different types of inorganic and organic pollutants. They are soluble or insoluble forms (2-3). They have increased the biogeochemical cycling of toxic heavy metals. That led to significant deposition of heavy metals in natural aquatic and terrestrial ecosystems (4). The heavy metals do not degradation and they are dropped, accustomed, or incorporated in water, sediment, and aquatic ecosystems. The heavy metals can be bioaccumulated and biomagnified by the food chain, and finally be assimilated by human consumers, resulting in health risks (5). When we exposure to heavy metals that lead to caus
different effects including growth inhibition, cancer, organ damage and nervous system damage. It is possible lead to death. The Pb, and Cd elements are toxic in the high and low concentrations (6-7). The removal process of heavy metals is essential point for all environmental safeguard agencies. The economic cost of treatment depending on volume, concentration of metals, and salinity and characteristics of wastewaters makes it impossible to do conventional technologies like precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, cementation, coagulation, flocculation, electrochemical treatment, membrane processes, and evaporation (8-10). The first imidazole was defined by Fischer (1882), and the nature of the ring system was established by Freud and Kuhn (1890) [11-12]. The imidazole ring is a essential of some important natural products, including purine, histamine, histidine and nucleic acid. It is present in the structure of many drug molecules, that is, azomycin 1 cimetidine 2 and metronidazole 3. Imidazole containing drugs have a broad scope in remedying various dispositions in clinical medicine [13-15]. His synthesis used glyoxal and formaldehyde in ammonia to form imidazole [16-20]. The azo- benzimidazole reagent is investigated in the sorption of Pb and Cd ions from their aqueous solutions under equilibrium conditions. Factors affecting the adsorption process were examined.

2. Materials and methods

Characterization

FTIR spectrum of the azo- benzimidazole reagent was recorded on TENSOR 27, Bruker spectrometer using KBr pellets. X-Ray Diffraction (XRD) of azo- benzimidazole reagent was taken on Powder PANalyti-cal X-Ray Diffractometer operating in reflectance mode at a Co–K _wavelength of 1.78897Å, over an angular range 2_ from 5° to 80° and a scan rate of 2°/min. The azo- benzimidazole reagent was synthesized by reacting 1 gram of 2-aminobenzimidazole in acidic condition at low temperature around zero with 0.5 gram of sodium nitrite to form diazonium salt of the benzimidazole. This salt was mixing with 1.2 gram of 2,4-dichlorophenol in basic condition to form the azo- benzimidazole reagent with 80% yield, violet powder.

3. Result and Discussion

3-1. The infrared ray and X-Rd powder of azo- benzimidazole reagent
The azo-benzimidazole reagent spectrum showed important diagnostic peaks as shown in Figure 1, the most important of which are: a peak at 3200 cm\(^{-1}\) and return to the amplitude vibration of N-H in the ring of the benzimidazole. It also showed a peak at 3063 cm\(^{-1}\) due to the stretching oscillation of the C-H. The vibration at 1734 cm\(^{-1}\) is due to the stretching vibration of the C=N group in benzimidazole ring. A peak at 1585 cm\(^{-1}\) refers to the (N= N) azo group C = C. As well as a peak at 1585 cm\(^{-1}\) is due for the C = C. The absorbances from 400 cm\(^{-1}\) to 1000 cm\(^{-1}\) are due to the bending absorbances of C-H.

The X-Rd powder spectrum of azo-benzimidazole reagent showed eight sharp signal which means the reagent of azo dye is crystal material as shown in Figure 2.

![Figure 1: Infrared spectrum of azo-benzimidazole reagent in KBr pellet](image-url)
3-2. Effect of acidity on the reacting azo-benzimidazole reagent with lead ion

The spectrum of azo-benzimidazole reagent was recorded in water as in the Figure 3 which showed absorption at 290 nm which is due to $\pi\rightarrow\pi^*$ and large absorption at 427 nm which is due to $n\rightarrow\pi^*$.

![Figure 3: UV-VISIBLE spectrum of Reagent in water at room temperature](image)

The UV-visible spectra of the reagent with lead ions were measured in water at the laboratory temperature at an acidic function pH= 2, where the absorption was 452 nm and under neutral medium pH=7, where the absorption was 476 nm, as well as at an basic function equal to pH=10, where the absorption was 543 nm as shown in the Figure 4. This means the best
absorption was at 543 nm in the basic medium, that is, when the proton removal process takes place from the reagent, which gives the detector power to interact with the metal ion.

![UV-VISIBLE spectra of the Pb-reagent in water at room temperature under different pH values](image)

**Figure 4:** UV-VISIBLE spectra of the Pb-reagent in water at room temperature under different pH values

**3-2-1. Mole Ratio of Lead ion with azo-benzimidazole reagent**

It is the molar ratio method (Mangsup and Chai: chit, 2003). It is the best and most widely used in determining the formula of metal ions with the reagents, as the absorbance of a series of solutions containing variable quantities of one component is measured by fixing the other component at (max) of the compound resulting from the interaction of the metal ion with the detector and the relationship between the absorption and the molar ratio is drawn. The mole ratio method was used at a wavelength of 543 nm in an aqueous solution by taking 2.5 mL of lead ion (lead (II) chloride) at a concentration of $10^{-4}$ molary (mole /litter) in all cases, while for the azo-benzimidazole reagent, 0.5 mL at a concentration of $10^{-4}$ molary was taken and mixed with 2.5 mL of lead ion solution. And then complete the volume to ten millilitres. Then we repeated the process with increasing 0.5 mL in each one as following: 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 ml were taken which depicted in Table 1. The absorption was plotted against the ratio of the volume of the reagent solution to the volume of the lead ion solution as shown in Figure 5. It was found that the ratio of the reaction of the detector with the metal ion (lead ions), is 2: 1, meaning two reagents correspond to one ion of lead.
Table1: number representing the absorption of lead-ion reagent solutions

| V reagent/V metal (Pb) | Absorbance |
|------------------------|------------|
| 0.2                    | 0.022      |
| 0.4                    | 0.072      |
| 0.6                    | 0.133      |
| 0.8                    | 0.187      |
| 1                      | 0.241      |
| 1.2                    | 0.297      |
| 1.4                    | 0.365      |
| 1.6                    | 0.43       |
| 1.8                    | 0.484      |
| 2                      | 0.523      |
| 2.2                    | 0.521      |
| 2.4                    | 0.523      |
| 2.6                    | 0.523      |
| 2.8                    | 0.53       |

Figure 5: Mole ratio of azo-benzimidazole reagent with Pb$^{2+}$

3-2-2. Calibration curve

The calibration curve was generated from the spectroscopic measurements made after determining the optimum parameters of the compound formed by the metal ion and the reagent as previously described. Give the calibration curve compliance of Beer-Lambert's law in the concentration range of 0.2 - 5 μg/mL of lead ion with equivalent concentration of
reagent under mole ration as shown in (Figure 6). The method turns out to be successful at low concentrations.

![Titration curve of lead with the azo-benzimidazole reagent](image)

**Figure 6: Titration curve of lead with the azo-benzimidazole reagent**

3-3. **Effect of acidity on the reacting azo-benzimidazole reagent with cadmium ion**

The UV-visible spectra of the azo-benzimidazole reagent with cadmium ions were measured in water at laboratory temperature as shown in Figure 7. At an acidic function of pH=2 and neutral (pH=7), as well as at a base function equal to (pH=10), where the absorption in all cases was 460 nm. A note worthy of attention, that there is high absorption (hyperchromic) in base medium and a decrease in absorption (the hypochromic) in acidic medium. Therefore the best condition is at the basic medium. That means the best absorption was at 460 nm in the basic medium due to remove proton from the reagent of azo dye, which gives the reagent a power to interact with the metal ion.
3.3.1. Mole ratio of azo-benzimidazole reagent to cadmium ions

The mole ratio method was used at a wavelength of 460 nanometres in aqueous solution by taking 2.5 mL of cadmium ion (cadmium (II) chloride) solution at a concentration of $10^{-4}$ molary (mole/L) in all cases, while for the reagent, 0.5 mL at a concentration of $10^{-4}$ mol/L was taken and mixed with 2.5 mL of cadmium ion solution. And then complete the volume to ten millilitres. Then we repeat the process with increasing 0.5 mL of reagent in every vase as following: 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, mL were taken which depicted in Table 2. The absorption was plotted against the ratio of the volume of the reagent solution to the volume of the cadmium ion with the reagent solution, and it was found that the ratio of the reaction of the reagent with the metal ion, equal to 2:1 reagent: cadmium as shown in Figure 8.

Figure 7: UV-VISIBLE spectra of the Cd$^{2+}$-azo-benzimidazole reagent in water at room temperature at different pH values (Acidic (black line), Neutral (violet) and basic (red line))
Table 2: number representing the absorption of lead-ion reagent solutions

| V reagent/V metal (Cd2+) | Absorbance |
|-------------------------|------------|
| 0.2                     | 0.033      |
| 0.4                     | 0.083      |
| 0.6                     | 0.162      |
| 0.8                     | 0.21       |
| 1                       | 0.301      |
| 1.2                     | 0.386      |
| 1.4                     | 0.452      |
| 1.6                     | 0.529      |
| 1.8                     | 0.652      |
| 2                       | 0.753      |
| 2.2                     | 0.76       |
| 2.4                     | 0.773      |
| 2.6                     | 0.785      |

Figure 8: Mole ratio of azo-benzimidazole reagent with Cd2+
3.3.2. Calibration curve of cadmium ions

The calibration curve was generated from the spectroscopic measurements made after determining the optimum parameters of the compound formed by the metal ion and the reagent as previously described. Give the calibration curve compliance of Beer-Lambert's law in the concentration range of 2-60 μg/mL as shown in (Figure 9). The method turns out to be successful at low and high concentrations.

![Figure 9: Titration curve of cadmium ions with the azo-benzimidazole reagent](image)

\[ y = 0.0098x + 0.0191 \]
\[ R^2 = 0.9983 \]

4. Conclusion

The reagent of azo-benzimidazole reagent is tridentate having high ability to coordinate to the metal ions like lead and cadmium. The azo-benzimidazole reagent can determine and remove large concentrations of cadmium in the range of 2-60 μg/mL and it can remove the concentrations of lead ions in the range of 0.2 - 5 μg/mL. The azo-benzimidazole reagent is crystalline material.
5. References

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