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Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite

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Abstract

Heavy metal pollution has become one of the most serious environmental problems nowadays. The removal of heavy metals from the environment is of special concern due to their persistence. Batch experiments were conducted to test the ability of activated carbon for the removal of lead, cadmium, nickel, chromium and zinc from water. The Langmuir and Freundlich adsorption isotherms were used to verify the adsorption performance. Nickel showed the highest removal percentages by activated carbon at all concentrations and the removal percentages decreased as the concentration of heavy metal increased. The obtained correlation coefficient (R^2) for different adsorbents suggested poor fitting of the experimental data to Langmuir isotherm for Cd, Pb, Ni, and Zn, while R^2 obtained using Freundlich model for different adsorbents indicated that it fitted the experimental data well. Silica/activated carbon (2:3) composite was more efficient in the removal of nickel ions than activated carbon and silica nanoparticles. SEM pictures were taken for the three particles under test.
Keywords: Adsorption; Isotherms; Heavy metals; nanoparticles; activated carbon; silica/activated carbon composites; silica.

1. Introduction

Heavy metals (Cadmium, Nickel, Lead and Chromium) which are natural components of the Earth's crust are usually associated with toxicity. Exposure to heavy metals, even at trace level, is known to be a risk for human

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beings [1]. The presence of zinc, cadmium, nickel and others metals in the aqueous environment has a potentially damaging effect on human physiology and other biological systems when the acceptable levels are exceeded [2]. Heavy metals cannot be degraded or destroyed. Heavy metal toxicity could result, for instance, from drinking-water contamination (e.g. lead pipes), increased ambient air concentrations near sources of emission, or ingestion via the food chain [3]. The increased use of heavy metals in industry has resulted in increased availability of metallic substances in natural water sources [4, 5]. Many technologies like adsorption, precipitation, membrane filtration, and ion-exchange have been used to remove metal pollutants from water [6]. However, adsorption has proven to be economical and efficient for removing heavy metals, organic pollutants and dyes from polluted waters [7]. Several adsorbents such as activated carbon, silica, and graphene can be used in the purification of water [4]. Activated carbon has shown to be an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. Because of its high surface areas that range from 500 to 1500 m^2 g^{-1} it is widely used in the treatment of wastewaters. The effectiveness of Activated carbon in cleaning up polluted water is due to its well developed porosity structure as well as the presence of a wide spectrum of surface functional groups. This makes it capable of distributing pollutants on its large internal surface, making them accessible to reactants [8]. Effectiveness of activated carbons to act as adsorbents for a wide range of contaminants is well noted [9].

The objective of the present work was to test the ability of activated carbon, silica and silica/activated carbon composites to remove heavy metals from water using batch adsorption method.

2. Materials & methods

All the reagents used in the present work were of analytical grade and obtained from Sigma-Aldrich. Activated carbon and standard solutions were also purchased from Sigma-Aldrich. The concentrations of heavy metals under study were determined by the atomic absorption technique type AA-6800, Shimadzo, Japan. Buffer solutions of pH 4, 7 and 9 for the calibration of pH-meters, and concentrated nitric acid (63%) were of high grade and obtained from Sigma and Fisher.

2.1. Preparation of activated carbon.

Activated carbon (AC) was modified by heat treatment [10] where it was washed with deionized water and then heated to 450°C for 4 hrs.
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2.2. Preparation of silica/AC (2:3) composite

The surface modification of SiO$_2$ with (3-Aminopropyl) triethoxysilane (APS) coupling agent was carried out in liquid phase. SiO2 powder (10 g) was firstly added to 150 mL ethanol, premixed and stirred for 30 min to get well dispersed SiO$_2$ suspension. After the addition of another 150 mL ethanol, 0.5 mL silane coupling agent APS was added into the suspension. The mixture was stirred, heated up to 50°C for 12 hrs, the obtained particles were filtered from the mixture, washed with ethanol and deionized water five times and dried under vacuum [11]. AC coated silica composite (SiO$_2$/AC) was prepared as silica/AC (2:3 W/W) ratio. Under mild magnetic stirring for 1 hr till the solutions became transparent, and AC precipitated with SiO$_2$-NH$_2$. The precipitate (SiO$_2$/AC) was collected and washed with water for several times to remove the unbound AC and afterwards dried under 60°C and ground before use.

2.3. Batch Adsorption Test on Activated Carbon

The adsorption of heavy metals by the adsorbents was studied using batch experiments. Twenty milligram of AC was added to 20 ml of different concentrations of heavy metal standard solutions (30, 50, 100 & 200 ppm), while the pH of the solution was adjusted to 2.0 using 1.0 N HCl. The solution was sonicated for 20 min. at 100 rpm and then allowed to cool and followed by equilibration at room temperature for 24 hrs. Solids were allowed to settle down and were removed using syringe filtration. The residual heavy metals were determined by atomic absorption spectrophotometer (AAS) analysis [12]. The adsorption isotherms were obtained by increasing the concentration of

heavy metal solutions from 50 up to 200 ppm. The removal percentage of the adsorbed heavy metal concentration was estimated followed the method adapted by Zabihi et al. [13]

Removal percentage: $= \frac{Ci-Ce}{Ce} \times 100$ (1)

Where C_i is the initial concentration (ppm), C_e is the concentration at final equilibrium (ppm). Adsorption data for adsorbate concentrations are described by Langmuir and Freundlich adsorption isotherms.

2.4.   *Removal of nickel by AC, Silica and silica/AC (2:3) composite*

Removal of nickel by AC, silica and silica/AC (2:3) composite was tested using the previously mentioned batch adsorption method, where 20 mg of the nanoparticles under test were supplemented one at a time to two flasks one containing 20 ml of 30 ppm Ni and the second containing 20 ml of 200 ppm Ni. The solutions were mildly sonicated for 20 min, and then allowed to cool followed by equilibration at room temperature for 24 hrs. Solids were allowed to settle down and were removed using syringe filtration. The residual heavy metals were determined by AAS. The results obtained were the mean of two trials.
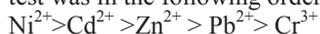
2.5.   *Characterization of the particles under test*

The microstructure of activated carbon, silica and silica/AC (2:3) composite were observed with scanning electron microscopy (TESCAN SEM, INCA). Nickel, cadmium and zinc adsorbed activated carbon samples were characterized using Fourier Transform Infrared Spectrophotometer (FT-IR) analysis and compared to the pure metal (Ni^{2+}, Cd^{2+} and Zn^{2+})(Shimadzu).

3.   Results & discussions

3.1. *Removal of heavy metals by activated carbon*

Data in Table 1 showed the effect of different metal concentrations (lead, cadmium, nickel, chromium and zinc one at a time) on the removal percentage of heavy metals. It was revealed that at low heavy metal concentration, the removal percentage was high and gradually decreased with the increase of heavy metal concentration. At 30 ppm of heavy metals, the removal percentages were 90, 86, 83.6, 83 &50.6, % for Ni, Cd, Zn, Pb & Cr respectively. At 30 ppm, Nickel was the metal with the highest removal percentage at all concentrations, followed by cadmium, zinc, lead then chromium which had the lowest removal percentage. On the other hand, the highest heavy metal concentration (200 ppm) led to the lowest removal percentage of the heavy metals under test (66.1, 69.6, 24, 84.1 and 74.9 % for Cd, Pb, Chr, Ni & Zn respectively). The obtained results in the present work concerning lead and cadmium agreed with that obtained by Tangjuank et al., [7].The removal percentage at 30 ppm for the metals under test was in the following order:
$Ni^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+} > Cr^{3+}$
The removal percentage for all the tested metals was the highest at 30 ppm and decreased with the increase in metal concentration. Erdem et al. [14] & Wu et al. [15] also reported that adsorption efficiency of metals decreased with increasing initial metal concentration. Ashtoukhy et al. [16] explained that at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled leading to less adsorption efficiency.
The FT-IR spectroscopic characteristics of the pure and adsorbed metals were shown in Table 2. IR spectra of the free metal salts and those adsorbed on AC surfaces supported adsorption of the metal cations on the surface; this was reflected in the shifts in wave numbers from 825 to 879.5 cm^{-1} for cadmium ions after adsorption with activated carbon; from 1112.93 to 1163.08 cm^{-1} for zinc ions and from 796.6 to 854.47 cm^{-1} for nickel ions. Therefore, the results of the present investigation revealed that after adsorption on activated carbon, there was an increasing shift for zinc followed by cadmium then nickel (50.15, 54.5 & 57.87 cm^{-1} $\Delta \bar{v}$ for Zn^{2+}, Cd^{2+} & Ni^{2+} respectively). These shifts indicated that there were binding processes taking place on the surface of activated carbon, and the greater the shift ($\Delta \bar{v}$) the stronger the bond between the activated carbon and the adsorbed metal [17]. This was compatible with the removal percentage data, where the removal efficiency was in the following order $Ni^{2+} > Cd^{2+} > Zn^{2+}$

Similarly and following the same trend, the order of $\Delta \bar{\nu}$ was as follows: $\Delta \bar{\nu} (Ni^{2+}) > \Delta \bar{\nu} (Cd^{2+}) > \Delta \bar{\nu} (Zn^{2+})$

Table 1: The removal percentages of metals with different initial concentrations using activated carbon.

Element	Initial concentration (C_i) (ppm)	Residual Concentration (C_e) (ppm)	Removal percentage (%)
Cadmium	30.00	4.00	86.00
	50.00	8.10	84.00
	100.00	30.20	70.00
	200.00	67.80	66.10
Lead	30.00	5.00	83.00
	50.00	13.00	74.00
	100.00	27.00	73.00
	200.00	60.80	69.60
Chromium	30.00	14.80	50.60
	50.00	25.90	48.20
	100.00	70.40	29.60
	200.00	151.90	24.00
Nickel	30.00	3.00	90.00
	50.00	6.10	87.80
	100.00	15.20	84.40
	200.00	31.80	84.10
Zinc	30.00	4.90	83.60
	50.00	9.40	81.20
	100.00	23.80	77.20
	200.00	50.20	74.90

Table 2. FT-IR results for pure metal ions and activated carbon adsorbed metals

Metal ion	Wave number $\bar{\nu}$ (cm^{-1})		
	$\bar{\nu}$ (Pure metal)	$\bar{\nu}$ (adsorbed metal)	$\Delta \bar{\nu}$
Ni^{2+}	796.6	854.47	57.87
Cd^{2+}	825	879.5	54.5
Zn^{2+}	1112.93	1163.08	50.15

In order to represent the equilibrium adsorptive behaviour successfully two kinds of several isotherms equations were tested to fit the experimental data [8, 18].

Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{b\theta} + \frac{C_e}{\theta} \qquad (2)$$

Freundlich equation

$$\ln q_e = \ln K + \frac{1}{n}\ln C_e \qquad (3)$$

Where,

$$q_e = \frac{C_i - C_e}{m} V \qquad (4)$$

Where q_e is the amount of metal ions adsorbed at equilibrium (mg.g⁻¹), C_i and C_e are the initial and equilibrium concentrations of metal ions in solution (mg.L⁻¹), m is the mass of adsorbent (mg), and V is the volume of the heavy metal solution (L). In the Langmuir equation, θ (mg.g⁻¹) is the measure of monolayer adsorption capacity under the experimental conditions and **b** (l.mg⁻¹) is Langmuir adsorption constant related to the energy of adsorption. These values can be obtained from the plot of C_e/qe against (C_e) [19]. Freundlich treatment gives the parameters, **n**, is the adsorption intensity and indicative of bond energies between metal ion and the adsorbent and **K**, is Freundlich constant with multilayer adsorption which related to bond strength and these values can be obtained from the plot of Ln q_e against Ln C_e. Moreover, the correlation coefficient R^2 values were used to obtain the best-fit linear equation [20,21]. The estimated model parameters with correlation coefficient (R^2) for the different models were shown in Table 3. The obtained correlation coefficient (R^2) for different adsorbents suggested poor fitting of the experimental data to Langmuir isotherm for Cd, Pb, Ni, and Zn. On the other hand, Langmuir isotherm was found to be applicable to the data of Cr indicating the formations of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The Langmuir monolayer adsorption capacity (θ) for chromium was found to be 60.9 mg/g with energy parameter of 0.02. The correlation coefficient (R^2) for different adsorbents indicated that the Freundlich model fitted the experimental data well. The values of 1/n<1 obtained for Cd, Ni, Zn and Cr ions indicates favourable adsorption.

Table 3. Estimated isotherm models and their constants values for AC adsorption of the different metals.

Heavy metal	Langmuir equation			Freundlich equation			
	R^2	$\theta_{(mg/g)}$	$b_{(l/mg)}$	R^2	K	1/n	n
Cadmium	0.87	178.5	0.03	0.98	12.18	0.54	1.84
Lead	0.70	294.11	0.01	0.97	7.244	1.38	1.42
Nickel	0.78	400	0.02	0.99	11.1	0.76	0.4
Zinc	0.82	344.82	0.01	0.99	7.414	0.75	2.00
Chromium	0.93	60.9	0.02	0.94	4.87	0.44	0.6

3.2. Removal of nickel by AC, Silica and silica/AC (2:3) composite

3.2.1. Batch adsorption test

The metal that had the highest removal percentage by AC was tested for its removal by silica and silica/ AC (2:3) composite by adsorption test. Table 4 showed the removal percentages of 30 & 200 ppm Nickel by different particles under test. Silica/AC (2:3) composite had the greatest removal percentage at 30 & 200 ppm (92.1 % & 87.6% respectively) followed by AC, then silica which had the lowest removal percentages among the tested particles (70.3 % for 30 ppm & 60.1 % for 200 ppm Nickel). It was worth noting that as the concentration of Nickel

increased, the removal percentages of the AC, silica and silica/AC (2:3) composite decreased. As reported by Tangjuank et al. [7] the increase in solution concentration leads to a decrease in adsorption of metals. This indicates that at high initial concentration of metal, the metal ions available to the surface of adsorbant are very high, so functional adsorption becomes dependant on initial concentration which was also stated by Ashtoukhy et al. [16] who explained that at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled.

Table 4. The removal percentages of nickel using AC, silica/AC (2:3) composite and silica.

Particle	Removal percentage of 30 ppm Nickel	Removal percentage of 200 ppm Nickel
AC	90.4	84.1
Silica	70.3	60.1
Silica/AC (2:3) composite	92.1	87.6

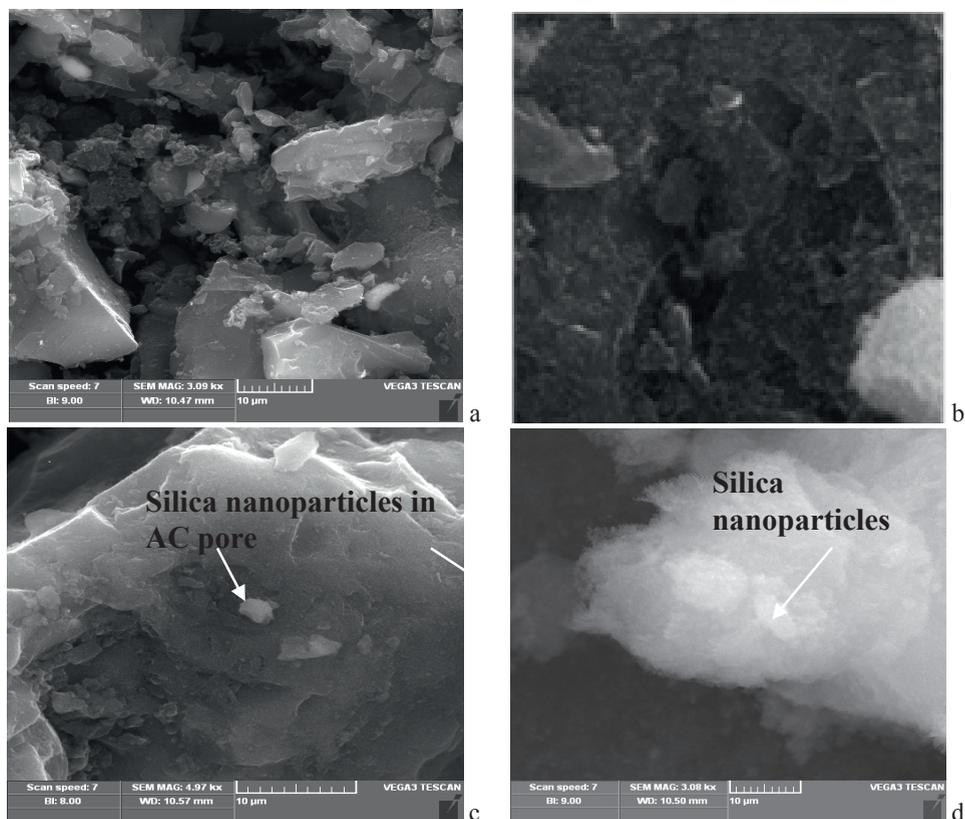*3.2.2. Characterization of the adsorbents under test*

Figure 1. Scanning electron micrographs of (a) AC, (b) silica/AC (2:3) composite at 1µm, (c) silica/AC (2:3) composite at 10 µm and (d) silica.

Fig. 1 illustrated the scanning electron micrographs of the particles under test at 1 & 10 μm magnifications. Analysis of the SEM image (Fig. 1a) revealed that activated carbon had a wide size distribution, with an average size of 25 μm, so it was considered as a microparticle. The silica/ AC (2:3) composite microstructure was shown in figures 1b & 1c, the macropores of activated carbon were clear on the surface of AC microparticle, while silica nanoparticles were indicated by arrows and had an average size of 12 nm. Figure 1d showed the pure silica nanoparticles appearing as white aggregates at 10 μm magnification.

4. Conclusions

In the present study, AC showed the greatest affinity towards nickel with 90 % removal percentage; the shifts in IR wave numbers reflected the bondings between AC and the adsorbed metals as presented by Freundlich isotherm. Silica/AC (2:3) composite showed the greatest removal percentage for 30 & 200 ppm nickel. SEM images revealed that AC was a microparticle with an average size of 25 μm, while silica were nanoparticles having an average size of 12 nm. Silica/AC (2:3) composite was the most effective microparticle for nickel removal and it is highly recommended to be used in water treatment for its high adsorptive capacity followed by AC and silica nanoparticles.

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