Study of impact of acids and comparison of adsorption efficiency of Pb(II) from carbon and its modified nano-nickel coated version
Tayyaba Asim, Riaz Ahmed and Muhammad Shahid Ansari

ABSTRACT

Acidic content in wastewaters poses greater difficulty in lead removal from most adsorbents as their removal efficiency significantly decreases in acidic media. Nano-nickel coated carbon (Ni/C), compared with uncoated carbon (C), has shown a much enhanced (almost 80% higher) tendency of Pb(II) removal from solutions having different acid concentrations. All of the characterization results show the creation of more active sites and functional groups on Ni/C. The pertinent kinetic models and thermodynamics of Pb(II) adsorption have demonstrated much improved efficiency by Ni/C. Various isotherms subjected to the sorption data revealed significant increase in the sorption capacities for Ni/C. The adsorption rates in acidic solutions were much higher for Ni/C. The temperature-dependent study enabled thermodynamic parameters to be worked out for C and Ni/C; for C the values are $\Delta H$: $19.4 \pm 0.5$ kJ·mol$^{-1}$, $\Delta S$: $76.1 \pm 2.1$ J·mol$^{-1}$K$^{-1}$, $\Delta G_{298}^\circ$: $-0.37 \pm 0.01$ kJ·mol$^{-1}$ while for Ni/C the values are $\Delta H$: $30 \pm 1$ kJ·mol$^{-1}$, $\Delta S$: $114 \pm 4$ J·mol$^{-1}$K$^{-1}$, $\Delta G_{298}^\circ$: $-4.56 \pm 0.02$ kJ·mol$^{-1}$. Both cases indicate endothermic, spontaneous and entropy-driven processes.

Key words | adsorption, carbon, kinetics, nano-nickel coated carbon, thermodynamics

INTRODUCTION

Lead is a very important and alarming toxicant affecting multiple body systems especially of children (Bose-O’Reilly et al. 2018). Due to inhalation and ingestion of lead particles, about 143,000 deaths per year have been reported particularly in developing regions. Although lead has been eliminated from various everyday utilities, due to its strengthening properties it is still used in cosmetics, paints, crystal vessels, ammunition, stained glass, traditional medicines and above all in drinking water delivery pipes and their joints in which lead solder is used (Wani et al. 2015). The wastewater streams mostly originating from these industries have higher amounts of lead. As a consequence of the creation and accumulation of acidic substances, effluent passages having pH in the acidic range present a huge hurdle in wastewater treatment (Ghasemi et al. 2014). The changing pH will also have a definite impact on the migration and distribution of heavy metals (Zhang et al. 2018). Adsorption is considered to be one of the most efficient as well as cost-effective methods for getting rid of heavy and toxic metals from water (Ince & Ince 2017). Although extraction, chemical precipitation, ion exchange and many others have been utilized for this purpose, they are either very expensive or cannot be applied on a large scale.

Wastewater reservoirs and streams present greater difficulty for getting lead removed through different adsorbents because the acidic content of these streams and huge amount of sludge produced as a result of the processes does not allow effective removal. To bypass this issue, nanotechnology can prove dynamic because of the high stability and greater adsorption capacity of the nanoparticles (Kahrizi et al. 2016). Nanoparticles due to their greater surface area and other properties are used for the efficiency enhancement of dye-sensitized solar cells (Lee et al. 2014), in hydrocarbon chemistry, hydrogen production and fuel cells. Lead has been adsorbed and removed by various materials (Rajput et al. 2016; Saleh 2016) including carbon (Asuquo et al. 2017) and carbon modified by different materials (Nekouei et al. 2015; Dashamiri et al. 2017). Ni/C does not deteriorate...
under rigorous conditions of acidic content and pH and hence the removal of heavy metals from wastewater streams can be brought about directly without any pretreatment (Asim et al. 2018).

In the present research, nano-nickel coated carbon (Ni/C) was synthesized and investigated for lead metal ion sorption and compared with carbon. The acidic content of aqueous solutions, buffers and various ions usually present in the natural water streams have also been studied to evaluate and compare the performance of adsorbents. The adsorption process onto C and Ni/C was optimized and kinetic as well as thermodynamic parameters evaluated for the process. Adsorption isotherms were compared for both the adsorbents and sorption energy values calculated for each.

**EXPERIMENTAL**

The chemicals (analytical grade) for this project were mostly acquired from Merck and Sigma Aldrich. Concentrated nitric acid in small amounts was used to dissolve PbO for preparing Pb(II) stock solution, the solution was heated up to dryness and later doubly deionized water was added. For each experiment the pH was adjusted according to the requirement. Carbon powder from Union Carbide having mesh size ≤ 100 was employed whose BET surface area came out to be 11.35 m²·g⁻¹ and was nuclear-reactor grade. The graphitic carbon was washed with a mixture comprising equal volumes of concentrated HCl and HF which followed drying at around 104 °C for 24 hours. Aqueous solution of 75 mL containing 0.727 g Ni(NO₃)₂·6H₂O was added to 5.00 g of the above treated carbon, the contents were allowed to equilibrate under argon for 30 minutes and subsequently water was distilled off (at ~180 °C) maintaining the inert atmosphere. The resulting black residue was heated to 210 °C for 15 minutes, cooled to ambient temperature, washed with water under argon and finally vacuum-dried at 100 °C for 18 hours. The expected value of this deposition was 3%, however the value for the present work turned out to be 2.85% ± 0.03% (Asim et al. 2018).

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis for the determination of the amount of nickel coated onto the carbon was done on a model 6500 (Thermo-Fischer Scientific, UK). X-ray diffraction (XRD) measurements were carried out on the instrument DS Discover from Bruker, Germany. A model Leo 440i microscope, Cambridge, UK, was used for scanning electron microscopy (SEM). Fourier transform infrared (FTIR) spectrophotometry was done by Bio-Rad Merlin FTIR3000MX while the voltammetry was carried out by a model 174A polarographic analyzer (Princeton Applied Research, NJ, USA). Atomic absorption spectrometry (AAS) for Pb analysis was done through Varian spectra AA300/400 (Australia).

A background electrolyte of 0.02 M HClO₄ was used to determine the concentration of Pb(II) through differential pulse anodic stripping voltammetry (DPASV). The initial potential was kept at −0.8 V, pulse amplitude at 50 mV and scanning rate at 10 mV/s with the Pb(II) ion peak appearing at about −0.38 V. As a comparison, a few samples were run on AAS and a ± 5% agreement was achieved for the above-mentioned techniques.

For the adsorption experiments, initially, 10 mL Pb(II) solution was shaken with 100 mg adsorbent. After shaking and centrifugation, the supernatant was subjected to DPASV so as to know the equilibrium concentration (Aₓ) of Pb(II). The sorption percentage and distribution coefficient (R_d) are given by the following relations, where A₀ is the initial Pb(II) concentration, V stands for volume of adsorbate and W is the weight of the sorbent:

\[
% \text{ sorption} = \frac{[C_i - C_f]}{C_i} \cdot 100 \tag{1}
\]

\[
R_d = \frac{[A_0 - A_e]}{A_e} \cdot \frac{V}{W} \cdot \text{cm}^2 \cdot \text{g}^{-1} \tag{2}
\]

**RESULTS AND DISCUSSION**

**Characterization of nano-nickel coated carbon**

According to XRD analysis results (Figure S1, available with the online version of this paper), the particle size D of deposited nickel found by the Scherrer equation is as follows:

\[
D = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \tag{3}
\]

where the source radiation has wavelength \( \lambda \) (1.5406 Å) and \( \beta_{1/2} \) is diffraction peak’s half-width appearing at the 2θ value of 44.64 for nickel. The nickel particles’ size deposited over carbon as evaluated by the equation is 8 nm.

Owing to the heat and chemical treatment during the process of depositing the nickel, a breaking down and hence a change in the morphology of carbon particles is seen in the scanning electron micrographs. According to the SEM X-ray analysis, a uniform distribution of nickel on the carbon (Figure S2(a) and S2(b), available online)
and around 8–10 nm size of nickel particles was observed. The results of the FTIR spectrum (Figure S3, available online) indicate a broad band between 2,950 and 3,650 cm⁻¹, which is usually characterized by bonded and free hydrogen and hydroxyl groups, and moreover, peaks between 1,180 to 1,350 cm⁻¹ depict the C-O of the carboxylic group and at 1,610 cm⁻¹ show the carbonyl group (Asim et al. 2018).

**Impact of acids**

Table 1 has the summary of the impact of acids in different concentrations over Pb(II) adsorption onto both sorbents. Since the pH of the solution is adjusted for each experiment and according to Table 2 the anions of the perchloric and nitric acids do not have a pronounced impact on the distribution coefficient values, therefore generally a trend is followed for both sorbents, i.e decreased $R_d$ with increasing acid concentration where it is more prominent for perchloric acid, nitric acid is mediocre and hydrochloric acid is last. Observing Table 2, it can be stated that this is purely an impact of the acidic media because for chloride the sorption of Pb enhances for both the cases. In all cases higher $R_d$ values are found, particularly for nitric acid, and almost 80% more removal efficiency is found for the Ni/C than for uncoated carbon. This kind of result proves Ni/C to be the better sorbent under the same optimized conditions.

**Dependence of pH**

Buffers ranging from pH 1 to 10 (Figure 1) show that maximum adsorption occurs at neutral pH, which can be correlated to the pH of natural water systems, and this indicates that for the removal of lead, carbon and Ni/C can be directly used in real systems.

**Kinetics of the sorption process**

The kinetics of the sorption process were evaluated by studying the adsorption under optimized conditions using different shaking times ranging from 1 to 25 minutes. Kinetic models were applied to Pb(II) sorption.

The Lagergren rate model (pseudo-first-order with $k_1$ (min⁻¹) as the rate constant) verifies the mass action phenomenon for the sorption of lead (Sivashankar et al. 2014). The following equations hold:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (4)

**Table 1 |** Impact of different acids in varying concentrations on the distribution coefficient $R_d$ for the sorption of 10 mL 4.82·$10^{-5}$ M Pb(II) onto 100 mg of carbon and nano-nickel carbon (Ni/C) at 298 K, with 30 min contact time.

| Acids and their conc. (M) in the sorptive medium | $R_d$ (cm²·g⁻¹) for Pb(II) onto |
|---|---|---|
| | Ni/C | Carbon |
| HClO₄ | 0.1 | 383 ± 3 | 283 ± 1 |
| | 0.01 | 421 ± 4 | 321 ± 1 |
| | 0.001 | 521 ± 5 | 501 ± 3 |
| HNO₃ | 0.1 | 238 ± 2 | 128 ± 1 |
| | 0.01 | 338 ± 4 | 194 ± 2 |
| | 0.001 | 434 ± 5 | 286 ± 3 |
| HCl | 0.1 | 174 ± 2 | 109 ± 1 |
| | 0.01 | 295 ± 3 | 198 ± 2 |
| | 0.001 | 321 ± 3 | 302 ± 2 |
| (Deionized water) | & 631 ± 3 | 525 ± 3 |

**Table 2 |** Comparison of monolayer adsorption capacities taken from the literature for Pb sorption using various adsorbents to the values calculated in the present work.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Monolayer sorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana peel</td>
<td>2.18</td>
<td>Anwar et al. (2010)</td>
</tr>
<tr>
<td>Bean husk</td>
<td>0.9895</td>
<td>Onwordi et al. (2019)</td>
</tr>
<tr>
<td>Mesoporous activated carbon</td>
<td>20.3</td>
<td>Asuquo et al. (2017)</td>
</tr>
<tr>
<td>Mn₃O₄ coated activated carbon</td>
<td>59.52</td>
<td>Lee et al. (2015)</td>
</tr>
<tr>
<td>Activated carbon from apple pulp</td>
<td>15.96</td>
<td>Depci et al. (2012)</td>
</tr>
<tr>
<td>Magnetic magnetite (Fe₃O₄) nanoparticle</td>
<td>53.11</td>
<td>Rajput et al. (2016)</td>
</tr>
<tr>
<td>Modified carbon nanotubes</td>
<td>100.0</td>
<td>Quyen et al. (2018)</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.86</td>
<td>This work</td>
</tr>
<tr>
<td>Nano-nickel coated carbon</td>
<td>34.3</td>
<td>This work</td>
</tr>
</tbody>
</table>
which can also be written as:

\[
\ln(1 - F) = -k_1 t
\]  

(5)

with \( F \) a fraction equalling \( q_t / q_e \), where \( q_t \) and \( q_e \) (mol·g\(^{-1}\)) are the amounts of Pb(II) adsorbed at time \( t \) and at equilibrium, respectively. The rate constants \( k_1 \) for sorption onto C and Ni/C come out to be 0.1967 and 0.495 min\(^{-1}\) while \( R^2 \) for both as determined by the plot turns out to be 0.9673 and 0.9905 respectively (Figure 2).

The following equation is of pseudo-second-order kinetics, which may also describe the sorption of Pb(II) on C and Ni/C (Sivashankar et al. 2014):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e^2}
\]  

(6)

where \( k_2 \) (g/μmol min) is the rate constant for second-order adsorption. Figure 3 shows the plots of \( t/q_t \) against \( t \) for obtaining the rate parameters; \( k_2 \) for C and Ni/C comes out to be 0.2514 and 0.91 g/μmol min and \( R^2 \) as 0.9936 and 0.9999 respectively. Comparing the results of the kinetic models, it can be stated that Pb(II) adsorption can be explained in a better way by the pseudo-second-order equation according to the correlation coefficients. In both the cases Ni/C shows a better rate of adsorption as compared with carbon alone, which shows that it is more suitable for Pb(II) removal.

Various equations as follows were applied to the adsorption kinetic data for evaluating the adsorption mechanism.

The Reichenberg equation for verifying the intraparticle diffusion mechanism was also applied (Raghav & Kumar 2019):

\[
F = \left(1 - \frac{6}{\pi^2}\right) e^{-Bt}
\]  

(7)

or

\[
Bt = -0.4977 - (1 - F)
\]  

(8)

Figure 2 | Plot of Lagergren model obtained varying contact times. (Rest of conditions are the same as for Figure 1.)

Figure 3 | Plot for second-order kinetic model obtained with varying contact times. (Rest of conditions are the same as for Figure 1.)

Figure 4 | Plot of Reichenberg equation obtained with varying contact times. (Rest of conditions are the same as for Figure 1.)

\[
B = \pi^2 D_i r^2 
\]  

\( D_i \) stands for the coefficient of inter-diffusion and the radius of the particle is represented by \( r \). Figures 2 and 4, respectively, show straight lines which do not pass through the origin for the plots of \(-\ln(1 - F)\) and \( Bt \) versus time, \( t \). For Ni/C the straight line deviates more from the origin, proving that in the overall kinetics of the adsorption process, film diffusion is not the limiting step. Different workers have observed a similar phenomenon while studying the double nature plots on various adsorption systems. According to Figure 4 the straight line passing close to the origin for C and not for Ni/C indicates that the rate-controlling step for C may be the intraparticle diffusion.

Further exploration of the probability of intra-particle diffusion was brought about by Equation (9), also known as the Morris–Weber equation (Largitte & Pasquier 2016):

\[
q_t = K_d t^{1/2} + I
\]  

(9)
The intraparticle diffusion rate constant is given by \(K_{d1}\) for the sorption of carbon and Ni/C respectively is given as 0.479 and 0.558 μmol/g min while \(I\) which directly indicates the boundary layer thickness, is 1.989 and 2.873 μmol/g. A small intercept value implies a smaller effect of the boundary layer and a larger value gives a greater effect. This information is acquired from Figure 5, which is drawn on the basis of Equation (9), and the \(R^2\) values for carbon and Ni/C are 0.9967 and 0.9839 respectively, having an initial linear portion for Ni/C which is due to the impact of boundary layer diffusion and a linear portion mainly due to intraparticle diffusion. As a general consequence of the deviation of the lines from the origin a proportionality between the resistance of the boundary layer and the intercept's magnitude to the extent of the thickness of the boundary layer is established. The values of \(K_{d2}\), \(I_2\) and \(R^2\) are 0.076 μmol/g min, 3.927 μmol/g and 0.8974 for the sorption onto Ni/C.

For Ni/C sorption of lead, in the beginning, the rate at which adsorption occurred was very fast, as the adsorption took place on the exterior surface of the sorbent. After saturation, lead ions moved through pores and thereby were adsorbed by the interior of the particles' surfaces. Consequently, due to diffusion resistance, the rate-determining step is intraparticle diffusion.

Predominantly, diffusion turns out to be the major mechanism of adsorption while intraparticle diffusion was mainly but not the only rate-determining process; boundary layer diffusion had a significant role in the rate-controlling step.

Adsorption models and adsorption capacity

The \(R_d\) values show that increasing the ions' concentration gradually decreases the sorption of Pb(II). This may be due to the saturation of the active sites thereby decreasing the overall number of active sites. These sorption data were used to evaluate adsorption isotherm models.

In order to find out whether the nature of adsorption was monolayer or multilayer the linear form of the Langmuir isotherm was applied (Azizian et al. 2018; Figure 6).

\[
\frac{C_e}{q_{ads}} = \frac{1}{M}b + \frac{C_e}{M}
\]

(10)

In Equation (10), \(C_{ads}\) is the adsorbed amount (mol·g\(^{-1}\)) and \(C_e\) is the equilibrium concentration (mol·L\(^{-1}\)) of Pb(II), \(M\) is a constant (also quoted as \(q_m\) in mg·g\(^{-1}\)depicting monolayer sorption capacity) which represents the maximum adsorption at a monolayer and the respective values as found from Figure 6 for C and Ni/C are 1.86 ± 0.02 and 34.3 ± 0.02 × 10\(^{-5}\) mg·g\(^{-1}\), the solute's binding energy is given by the constant \(b\), which varies with temperature and is related to the change in the adsorption's enthalpy, the values of which are 11.5 ± 0.3 × 10\(^4\) and 5.9 ± 0.3 × 10\(^4\) L·mol\(^{-1}\), and the \(R^2\) values from the figure are 0.9888 and 0.994 respectively.

Using literature values and comparing monolayer sorption capacities of Pb onto various adsorbents, it is evident from Table 2 that carbon without treatment gives values close to what the natural adsorbents like banana peel and bean husk would render. However nano-nickel coated carbon gives higher values (mg·g\(^{-1}\)) of the sorption capacity than some (not all) of the other adsorbents which have been modified either via coating with other materials, activation or nanotechnology. The focus of the present work remains that the adsorbents while giving better sorption capacities must not deteriorate while undergoing the process of adsorption under acidic and various pH conditions.

The linear version of the Freundlich isotherm is given below (Bordoloi et al. 2017):

\[
\log C_{ads} = \log C_m + \frac{1}{n} \log C_e
\]

(11)

where \(C_{ads}\) and \(C_e\) are adsorbed and equilibrium concentrations while \(C_m\) and 1/\(n\) are constants. Figure 7 depicts

Figure 5 | Morris-Weber plot obtained with varying contact times. (Rest of conditions are the same as for Figure 1.)

Figure 6 | Langmuir isotherm for the sorption of varying concentrations of 10 mL Pb(II) solution, onto 100 mg of carbon and nano-nickel carbon (Ni/C) at 298 K, with 20 min contact time.
the linear plots, plotted using the Freundlich equation; the sorbent surface heterogeneity and its adsorption capacity are given by $1/n$ and $C_m$ respectively; higher surface heterogeneity is observed with greater fractional values of $1/n$, which for carbon and Ni/C respectively are 0.35 and 0.64, while higher $C_m$ values represent higher capacity and are found to be $0.21 \pm 0.04$ and $8.24 \pm 0.9$ mmol g$^{-1}$. The $R^2$ values as represented by Figure 7 are 0.96 and 0.9866 for carbon and Ni/C respectively. As a result of the higher catalytic activity of the Ni/C there is an almost 30-fold increase of the adsorption in comparison to carbon.

The linear form of the Dubinin–Radushkevich (D-R) isotherm is applied to the sorption process (Bordoloi et al. 2017):

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2$$

(12)

$X_m$ is the maximum adsorption capacity in (mol·g$^{-1}$), $\beta$ (kJ$^2$·mol$^{-2}$) is a constant, related to the sorption energy; the Polanyi potential $\varepsilon$ for adsorption is given as:

$$\varepsilon = R \cdot T \cdot \ln(1 + C_{eq})$$

(13)

with gas constant $R$ (kJ·mol$^{-1}$), temperature $T$ (K) and $C_e$ with the usual meaning. Figure 8 has the D-R plots for carbon and Ni/C and the $R^2$ values are 0.9879 and 0.9982 respectively. The respective values of $\beta$ for carbon and Ni/C are $0.0025 \pm 0.0001$ and $41 \pm 0.0001$ kJ$^2$·mol$^{-2}$ while those of $X_m$ are $29 \pm 2$ and $187 \pm 12$ μg·mol$^{-1}$. There is a six-fold increase of maximum sorption capacity values for Ni/C, which indicates enhanced catalytic activity compared with C. If the sorbent surface is overall heterogeneous in nature but assuming the extremely small sub-regions of the sorbent surface to be structurally uniform and energetically homogeneous, the Langmuir isotherm as an approximation is chosen to be the local isotherm; then the sorption energy $E$ can be related to the constant $\beta$ by the following relation:

$$E = \frac{1}{\sqrt{-2\beta}}$$

(14)

where $E$ is the free energy of the process when a mole of solute transfers from infinity to the surface of the sorbent. Physical adsorption is depicted if the numerical values of $E$ lie between 1 and 8 kJ·mol$^{-1}$, however, above this range chemical adsorption exists. For carbon and Ni/C, the respective $E$ values of $14.3 \pm 0.3$ and $11.4 \pm 0.1$ kJ·mol$^{-1}$ indicate predominantly chemisorption.

**Temperature dependence of Pb(II) adsorption**

Adsorption can considerably be influenced by temperature, whereby increasing the temperature results in the speeding up of various steps involved in adsorption including the creation of a greater number of active sites and increased diffusion of the sorbate. Figures 4 depicts the relationship of temperature and equilibrium constant where the latter is calculated through the following relation:

$$K_c = f/(1 - f)$$

(15)

and $f$ represents the fraction of the adsorbed Pb(II). Various thermodynamic parameters can be evaluated using the following equations:

$$\Delta G = -RT \ln K_c$$

(16)

$$\log K_c = -\Delta H/2.303 RT + \Delta S/2.303R$$

(17)

where $\Delta G$, the Gibbs free energy, for carbon and Ni/C respectively is $-0.37 \pm 0.02$ and $-4.56 \pm 0.05$ kJ·mol$^{-1}$;
Table 3 | Impact on the sorption process due the presence of some common ions in water; the optimized conditions of sorption include vol. – 10 mL, Pb(II) conc. – 4.82·10⁻⁴ M, weight of both sorbents – 100 mg at 298 K, with 20 min contact time

<table>
<thead>
<tr>
<th>Common ions present</th>
<th>$R_d$(cm²·g⁻¹)</th>
<th>Carbon</th>
<th>Ni/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (optimum condition)</td>
<td>525 ± 3 (15 min)*</td>
<td>631 ± 3 (12 min)*</td>
<td></td>
</tr>
<tr>
<td>Sodium (Na⁺)</td>
<td>515 ± 5</td>
<td>632 ± 4</td>
<td></td>
</tr>
<tr>
<td>Potassium (K⁺)</td>
<td>514 ± 4</td>
<td>639 ± 5</td>
<td></td>
</tr>
<tr>
<td>Zinc (Zn²⁺)</td>
<td>790 ± 7</td>
<td>513 ± 4</td>
<td></td>
</tr>
<tr>
<td>Copper (Cu²⁺)</td>
<td>626 ± 5</td>
<td>460 ± 3</td>
<td></td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>458 ± 4</td>
<td>498 ± 4</td>
<td></td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>588 ± 6</td>
<td>682 ± 5</td>
<td></td>
</tr>
<tr>
<td>Cadmium (Cd²⁺)</td>
<td>599 ± 6</td>
<td>515 ± 4</td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr³⁺)</td>
<td>537 ± 6</td>
<td>413 ± 4</td>
<td></td>
</tr>
<tr>
<td>Uranium (U³⁺)</td>
<td>486 ± 4</td>
<td>659 ± 6</td>
<td></td>
</tr>
<tr>
<td>Selenium (Se⁴⁺)</td>
<td>488 ± 5</td>
<td>308 ± 3</td>
<td></td>
</tr>
<tr>
<td>Nitrate (NO₃⁻)</td>
<td>520 ± 5</td>
<td>638 ± 4</td>
<td></td>
</tr>
<tr>
<td>Chlorate (ClO₄⁻)</td>
<td>530 ± 2</td>
<td>628 ± 3</td>
<td></td>
</tr>
<tr>
<td>Bicarbonate (HCO₃⁻)</td>
<td>457 ± 5</td>
<td>576 ± 5</td>
<td></td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>885 ± 7</td>
<td>787 ± 6</td>
<td></td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>636 ± 6</td>
<td>615 ± 5</td>
<td></td>
</tr>
<tr>
<td>Iodide (I⁻)</td>
<td>486 ± 3</td>
<td>583 ± 4</td>
<td></td>
</tr>
<tr>
<td>Carbonate (CO₃²⁻)</td>
<td>328 ± 3</td>
<td>315 ± 3</td>
<td></td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td>369 ± 3</td>
<td>313 ± 3</td>
<td></td>
</tr>
<tr>
<td>Oxalate (C₂O₄²⁻)</td>
<td>457 ± 9</td>
<td>388 ± 3</td>
<td></td>
</tr>
</tbody>
</table>

*Respective optimum time for gaining equilibration.

$\Delta S$, the entropy change for the process of sorption and its respective values, is 76 ± 2 and 114 ± 4 J·mol⁻¹·K⁻¹; and $\Delta H$ depicting the enthalpy changes has the respective values of 19.4 ± 0.5 and 30 ± 1 kJ·mol⁻¹. The entropy-driven sorption process on both the sorbents is more spontaneous in the case of Ni/C.

Interference of other ions

Since in the natural water streams, there are many other ions present to interfere with the adsorption process, for studying any such influence cations were added to the optimized adsorption set-up as nitrates and anions as sodium salts while keeping their concentrations 10-fold that of the Pb(II) as both these had no plausible impact on Pb(II) sorption.

Table 3 shows that a decrease in lead adsorption for both the sorbents is observed by the addition of SO₄²⁻, C₂O₄²⁻, Mg²⁺, HCO₃⁻, Se⁴⁺, I⁻, S²⁻, and CO₃²⁻. However, enhancement in the process for both cases is seen for Cl⁻, Br⁻ and Ca²⁺.

The presence of Cu²⁺, Zn²⁺, Cr³⁺ and Cd²⁺ increased Pb(II) sorption onto C but decreased it on Ni/C, while U³⁺ and K⁺ had an opposite impact. The reason for this variety of behaviour may be due to competition between Pb(II) and these ions. Some of the anions which suppress sorption may do so because of the formation of more stabilized anionic-type complexes with Pb(II) having a lesser affinity of sorption towards the sorbent. Also, there is a possibility that these complexes may not adsorb at all and hence a clear-cut reduction of Pb(II) sorption in their presence. Probably, increase in the sorption may be due to the creation of an environment where more sites having equal energy is somehow available for the sorption (Asim et al. 2019).

CONCLUSIONS

Ni/C is more stable and shows better recovery in acidic media than carbon alone. Nano-nickel coating of the carbon proves an enhancement in Pb(II) adsorption from aqueous solutions as the adsorption capacities and rates increase manifold on Ni/C than carbon. Kinetically the sorption process is better explained by a second-order equation. The chemical nature of the sorption process is confirmed by adsorption energy calculated via D-R isotherms. The calculated thermodynamic parameters confirm the spontaneous nature of the process.

REFERENCES


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