Determination some Heavy metals in Sediments of Shatt Al-Hilla River by Using Modified Single Chemical Fractionation Technique

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Abstract
Surfacial sediment composite samples were collected from six main sampling stations at Shatt Al-Hilla River from Khafaja area to Betta bridge in Babylon province.

A four-step modified single sequential extraction procedure was used to determine heavy metal (Pb,Ni,Fe and Cu) chemical phases in the sediment samples.

The results showed that there was concentrated for the high values of total concentrations of studied heavy metals in the station (5). When comparing the percentage of heavy metals in exchangeable and carbonate fractions at studied stations with risk assessment code we noted that the Ni,Fe and Cu were located within the degree: No risk. while Pb metal was within the degree: Low risk which indicates the dominance of anthropogenic sources effect.

Introduction

Heavy metals in aquatic systems are removed from the water column by interacting with particulate or organic matter, and are deposited as sediments (Puig et al.,1999; Tang et al.,2008).

It is essential to distinguish and quantify the various forms of metals to yield a better understanding of potential and actual environmental impacts of contaminated sediments (Sakan et al.,2007). Sediment constitutes the most important sink of metals and other pollutants, it can act as a nonpoint source and have the potential to release the sediment-bound metals and other pollutants to overlying waters, and in turn adversely affects aquatic organisms (Wang et al.,2004)

In the bottom sediments, the distribution of heavy metals is affected by mineralogical and chemical composition of suspended material, anthropogenic influences, and in situ processes such as deposition, sorption, enrichment in organism, etc. (Forstner and Muller,1975; Jain et al., 2005)

The behavior of the elements in the environment (bioavailability, toxicity, and distribution) cannot be reliably predicted assuming their total concentration (Alomary
and Belhadj 2007). The potential environment risk of heavy metal in sediments depends on both its total content and speciation. In fact heavy metals have different chemical forms in sediments (Jing et al., 2009). Sequential extraction is an important and widely applied tool for gaining information on potential mobility (hence, potential bioavailability and toxicity) of potentially toxic metals in the environment (Dubravka et al., 2010).

The aim of this paper is to study the sediments pollution with different types of heavy metals found along with the chemical forms and to assess their toxicity in the river by using the risk assessment code.

Material and Methods
Sediment sampling
Surfacial sediment composite samples were collected from six main sampling stations at Shatt Al-Hilla River from Khafaja area to Betta bridge in Babylon province. All samples were transferred in labeled bags. Sediment samples were air-dried, ground, passed through a 2mm sieve, and carefully preserved until laboratory analysis.

characteristics of Sediments
Sediments pH and EC were measured in 1:2 sediment water suspension (Jackson, 1973). Organic matter content was determined following modified Walkley and Black’s method (1936) as described by Jackson (1973). Total Carbonate in sediment samples was measured by acid neutralization method as described by Schollenberger (1945). The proportions of sand, silt and clay-sized particles were determined according to (Day, 1965).

Modified single sequential extraction technique
A four-step sequential extraction procedure was used to determine heavy metal fractions (chemical phases) in the sediment (Badri and Aston, 1983; Ismail and Ramli, 1997). The method is modified and designed to separate the heavy metal into four fractions.

(1) Fraction 1: Easily, freely or leachable and exchangeable (EFLE). About 5 g of sample was continuously shaken for 3 h with 25 ml 1.0M ammonium acetate (NH₄CH₃COO), pH 7.0 at room temperature.

(2) Fraction 2: metals bound to carbonate. 5 g of sample was continuously shaken for 5 h with 25 ml 1.0M ammonium acetate (NH₄CH₃COO), pH 5.0 at room temperature.

(3) Fraction 3: Oxidisable-organic. 5 g of sample was first oxidized with 7.5 ml H₂O₂ (R&M Chemicals 35%) in a water bath at 90°C. After cooling, the metal released from the organic complexes was continuously shaken for 3 h with 25 ml of 1.0M ammonium acetate (NH₄CH₃COO) acidified to pH 2.0 with HCl, at room temperature.

(4) Fraction 4: Residual. Metals in this fraction is mainly fixed in the primary and secondary minerals (Wu et al., 2004). 5 g of sample was digested in a 5 ml combination (ratio of 4:1) of concentrated HNO₃ (AnalaR grade, R&M Chemicals 65%) and HClO₄ (AnalaR grade, R&M Chemicals 70%).
Results and discussion
Sediment characteristics

Table 1 showed the characteristics of sediment under study, which related to the speciation of studied heavy metals in surfacial sediments. The pH values of the river sediments slightly varies from 7.8 to 8.1 indicating that the sediments were weakly alkaline. The EC values varies from 0.86 to 12.27 dS.m\(^{-1}\). The maximum value of 12.27 dS.m\(^{-1}\)of EC at station 6 indicating the anthropogenic influences on the sediment quality (Zhan et al., 2010) specially agricultural and domestic activities in Hilla city. Organic matter, and carbonate (CaCO\(_3\)) are of good correlation with the chemical fractions of trace metals. Metals are easy to combine with organic matter and carbonate (Wang et al., 2010). Organic matter, CaCO\(_3\), are within the range of 0.16 % to 0.25 % and 23.2 to 32.0%, respectively.

The Results showed that the main component of surfacial sediment was silt + clay, with a range from 52% to 78%. Station 4, 2 and 5 had the highest silt + clay contents whereas station 1 and 6 had relative low silt + clay contents.

Table 1. Sampling stations and some characteristics of Surfacial sediments of Shatt Al-Hilla River.

<table>
<thead>
<tr>
<th>Stations</th>
<th>pH</th>
<th>EC dS.m(^{-1})</th>
<th>O.M %</th>
<th>Carbonate%</th>
<th>Silt +Clay%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.9</td>
<td>0.86</td>
<td>0.18</td>
<td>23.2</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>7.9</td>
<td>1.27</td>
<td>0.20</td>
<td>23.8</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>7.8</td>
<td>3.22</td>
<td>0.25</td>
<td>32.0</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>7.9</td>
<td>1.26</td>
<td>0.16</td>
<td>25.0</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>8.1</td>
<td>1.03</td>
<td>0.18</td>
<td>27.7</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>7.9</td>
<td>12.27</td>
<td>0.22</td>
<td>24.5</td>
<td>55</td>
</tr>
</tbody>
</table>

Heavy Metal Fractionation

Figure (1-8) show the concentrations (in ppm) and percentage (%) of heavy metal (Pb, Ni, Fe and Cu) chemical fractions in surfacial sediments at study stations respectively.

Lead is a naturally occurring element that has no recognized essential biological function; yet it is toxic to almost all organisms. Recognition of its toxicity appears to date back to Hippocrates, and the clinical effects have been recognized for centuries (Rajeshwa and Ibanez 1997).

In this study, the total concentration (ppm) of Pb is in the range of 18.5 (station 2) to 27.06 (station 5). In the fraction 1 ranged from 0.35 (station 2) to 2.7 (station 5) with percentage of 4.76% at all studied stations. In the fraction 2 ranged from 0.66 (station 5) to 1.3 (station 6) with percentage of 4.88%. In the Fraction 3 ranged from 5 (station 1) to 7.8 (station 6) with percentage of 30.8%. In the fraction 4 ranged
from 10(station 3) to 17.5(station 1) with percentage of 59.48%. The percentage of fraction 1 and 2 at all stations (9.64).

Nickel is generally considered to be an essential trace element. It is subject to homeostatic regulation and mobilization in response to disease and physiological stress, and its absence or lack in the mammalian organism produces well-defined deficiency symptoms (Nieboer et al., 1988).

The total concentration (ppm) of Ni is in the range of 114.5(station 3) to 140.5(station 5). In the fraction 1 ranged from 0.3(station 6) to 0.8(station 2) with percentage of 0.42%. In the fraction 2 ranged from 0.4(station 6) to 4.2(station 1) with percentage of 1.9%. In the fraction 3 ranged from 9.7(station 6) to 11.2(station 1) with percentage of 8.42%. In the fraction 4 ranged from 100.2(station 3) to 127.9(station 5) with percentage of 89.25%. The percentage of fraction 1 and 2 at all stations (2.35).

Iron is the most important metal and one of the major constituents of the lithosphere. Fe plays a special role in the behavior of several trace elements and is in the intermediate position between macro- and micronutrients in plants, animals and humans (Kabata-Pendias and Arun 2007).

The total concentration (ppm) of Fe is in the range of 629.0(station 4) to 1228.9(station 6). In the fraction 1 ranged from 0.2(station 2 and 4) to 1.0(station 1) with percentage of 0.04%. In the fraction 2 ranged from 2.7(station 5) to 6.9 (station 2) with percentage of 0.41%. In the fraction 3 ranged from 4.1(station 1) to 29.3(station 6) with percentage of 1.22%. In the fraction 4 ranged from 620.8(station 4) to 1193.6(station 6) with percentage of 98.26%. The percentage of fraction 1 and 2 at all stations (0.45).

Copper is one of the oldest known metals and is the 25th most abundant element in the Earth’s crust. Prior to the identification of copper as a micronutrient, it was regarded as a plant poison. Therefore, no discussion of copper toxicity can rightfully begin without mention of its use as fungicide (Reuther et al., 1966; Barker and David 2007).

The total concentration (ppm) of Cu is in the range of 8.21(station 6) to 21.8(station 5). In the fraction 1 ranged from 0.05(station 4) to 0.23(station 5) with percentage of 0.88%. In the fraction 2 ranged from 0.10(station 1) to 0.22(station 5) with percentage of 1.25%. In the fraction 3 ranged from 0.3(station 1 and 3) to 0.75(station 5) with percentage of 3.8%. In the fraction 4 ranged from 7.2(station 6) to 20.6(station 5) with percentage of 94.06%. The percentage of fraction 1 and 2 at all stations (2.12).
Fig. 3 Concentration (ppm) of nickel at study stations

Fig. 4 Chemical fractionation of nickel as % at study stations

Fig. 5 Concentration (ppm) of iron at study stations

Fig. 6 Chemical fractionation of iron as % at study stations

Fig. 7 Concentration (ppm) of copper at study stations

Fig. 8 Chemical fractionation of copper as % at study stations
It is clear from the results of modified single chemical fractionation technique used to determination Heavy metals(Pb,Ni,Fe and Cu) in Sediments of Shatt Al-Hilla River there was concentrated for the high values of total concentrations (the sum of all fractions) of studied heavy metals in the station (5) which is located near the center of Hilla city may be attributed to the anthropogenic activities (terrestrial inputs) such as agricultural and domestic discharges rather than the natural rock weathering effect.

The total concentrations of heavy metals(Pb,Ni,Fe and Cu) at present study are less than those obtained by Al-Taee (1999) when she studied the trace elements in the sediments of Shatt Al-Hilla has due to the stopover of industrial activity in areas of Musayyib and Al-Sadaa in the years followed the previous study due to wars, which reflected on the quantity and quality of solid and liquid loaded with pollutants that spilled in Shatt Al-Hilla.

Recently, it is widely accepted that the role of aquatic sediments as a sink or as a source of pollutants cannot be fully assessed by measuring total metal concentrations, because the chemical form of the metal in the sediment determines behaviour and remobilization in the environment. By studying the distribution of the metals between the different phases, their contamination risk can be found out (Jain et al., 2010).

Jain et al., (2010) reported that the evident from the results of the fractionation study that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment. Exchangeable and carbonate bound metals are weakly bound to sediment components and may be equilibrate easily with the aqueous phase, and is considered more mobile and dangerous than other fractions (Moalla et al., 1997; Wang et al., 2010).

The risk assessment code indicates the sediment which can release heavy metal in exchangeable and carbonate fractions; % of the total concentration < 1: No risk, will be considered safe for the environment, 1–10: Low risk, 11–30: medium risk, 31–50: high risk, >50: very high risk, and can easily enter the food chain (Perin et al., 1985):.

When comparing the percentage of heavy metals(Pb,Ni,Fe and Cu) in Exchangeable(fraction 1) and carbonate fractions(fraction 2) at studied stations with risk assessment code we noted that the Ni,Fe and Cu were located within the degree: No risk. while Pb metal was within the degree: Low risk which indicates the dominance of anthropogenic sources (Jain et al., 2010).
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