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*Full Length Research Paper*

# Heavy metal ions adsorption by suspended particle and sediment of the Chalus River, Iran

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**Nowadays, it is important to evaluate the self-purifying capacity of rivers because of the different kinds of pollutants discharged into them. Important kind of pollutants and heavy metals exist in wastewaters industries. When the Sorb Dona mine is placed in Upper Chalus River, in the west of Mazandaran, products of mine wastewater are discharged into the river, making this important and protective river to encounter serious environmental risk. This research evaluates procedures of eliminating heavy metals existing in mine wastewater of the Sorb Dona when Chalus River flow is muddy. For forming muddy flow in laboratory, according to previous results, there are uptake of samples of sediments and river water from three hydrometer stations namely Vali Abad, Pole Zoghal and Masab. After preparing samples in the laboratory, standard metals including Pb, Cu, Zn and Fe (15, 5, 5, and 5 mg/l, respectively) and sediments from the three stations, both arranged in the concentrations of 1000, 3000, 7000, and 11000 mg/l, increased the samples of river water; and then they are mixed in JAR TEST apparatus twice for one and the half hour until adsorbing amount of heavy metals in sediments is evaluated. The results obtained from the elimination of heavy metals (Pb, Cu, Zn, and Fe) from sediments show that the amounts of these eliminated metals in the concentration of 11000 mg/l arrangement are equal to 84.38, 85.36, 32.4, and 93.74%. Also, results of contact times showed that contact time of efficiency is rarely one hour ahead.**

**Key words:** Chalus River, adsorption, heavy metal, suspended particle, sediment.

## INTRODUCTION

There are close relationships between heavy metal ions and sediments, such as suspended particles, bed loads and bottom sediments in river water. River sediments adsorb most of the heavy metal ions from the water (Zhou and Kot, 1995). In recent years, several researchers have been investigating the adsorption of heavy metal ions onto river sediments or soils (Lee, 2003; Korfali and Davies, 2005; Salim, 1983; Xiaoyuon, 1983). For instance, Xiaoyuon (1983) monitored the adsorption of heavy metal ions such as Cu, Zn and Ni onto sediments in the Jionshajing River and the results showed that pH of river water is an important factor. In all, experimental results showed that carbon is the main factor to determine the adsorption value of heavy metal onto sediment (Xiaoyuong, 1983). Obasohan et al. (2007) have monitored the post-dredging concentrations of Cu, Mn, Zn, Cr, Ni and pb in the water, sediment and in freshwater mudfish, *Clarias gariepinus*, from the Ikpoba River in Benin City, Nigeria.

The results showed that pb levels of Mn, Ni and pb in water and Cu, Mn, Cr and in fish were higher than the recommended levels in drinking water and food fish and could pose health hazards (Obasohan et al., 2007). Salim (1983) has also studied the effects of chemical composition and particle size of suspended matters in river water on the adsorption of lead onto these particles. Saeedi et al. (2004) have studied the role of riverine sediment and particulate matter in adsorption of heavy metals. The results of the analysis showed that riverine

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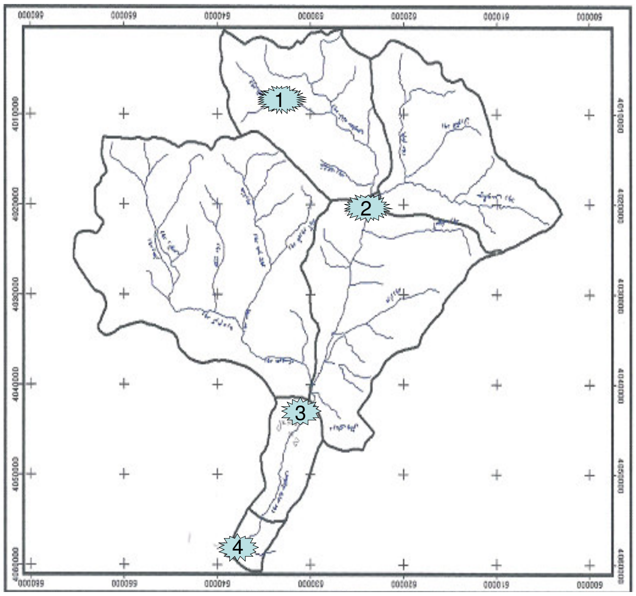


**Figure 1.** Situation of stations: (1) Sorbs orb Dona Mine; (2)Vali Abad; (3) Pole Zoghal and (4) Masab.

bottom sediments have greater potential for adsorbing heavy metals than suspended matters. However, the trend of adsorption sediments and suspended matters were similar. In addition, results revealed that increasing concentration of metal would cause desorbing cadmium onto sediments and suspended matters (Saeedi et al., 2004).

Other researchers have studied adsorption properties of sediments with respect to heavy metal on the Hindon River. Results showed that factors including diameter of particles, number of ions, Fe and Mn oxides and pH of river water and sediment are also important.

There are many rivers in the North of Iran. One of the largest and important rivers is Chalus River, located in the Mazandaran Province. Many active industries like Dona Sorb mine are near and upstream this river. The Chalus City is located near the Caspian Sea and downstream the Dona Sorb mine. Thus, the Chalus River received mainly waste and wastewater containing heavy metal ions due to the activity of the Dona Sorb mine. On the foundation last studied, the important factors of waste bp of the Dona mine were heavy metal ions including BP, Zn, Cu, Fe and other heavy metal with traces of Sorb. The Chalus River is a river with a high concentration of sediments. In flood times, the concentration of sediment is more than twenty kilograms per cubic meter. The concentration of sediment is high and the diameter of sediment is small. The concentration of suspended particle is low under normal conditions. It is important to study, the adsorption capacity of heavy metal ions onto suspended particles and sediment to set up water quality models for heavy metal ions and to determine their pollutant tolerance. Theretofore, the aim of this paper was to pb the experimental adsorption of heavy metal ions, such as Sediments Chalus River suspended particle and sed0069ments. In this research, environmental factors, such as heavy metal ions concentration and suspended particle and sediment concentrations, particle diameter and contact times were evaluated to provide more information that will enhance suitable isotherm for removal of simulation of heavy metal ions in the Chalus River.

## STUDY REACHED BACKGROUND

The Chalus River is a river with high water, situated completely at mountainous region and its head has sprung over the four hundred meters height in centeral Alborz famous to Kandevan. The main branches of Chalus River are Kandevan, Elia and Angoran.

The area of basin of the Chalus River is approximately equal to 1710 $Km^2$ with perimeter equal to 230 Km. In result, length of equivalent rectangle is equal to 91.3 Km and width of equivalent rectangle is equal to 18.7 Km. The average basin slope with Horton method is equal to 37% and average slope of the Chalus River is equal to 4.7%. The maximum highest basin of the Chalus River has 4150 m of free level sea surface. The average level of basin of the Chalus River has 1950 m of free level sea surface.

The Chalus River pollutant sources are generally divided into three categories: sanitary wastewater, agriculture wastewater and industrial wastewater. The important source of pollutant of industrial wastewater onto the Chalus River is Sorb Dona mine.

The Sorb Dona mine with height of about 3300 m of free level sea surface is situated at 92 km in Chalus City and is over thirty years.

The nominal capacity of the Sorb Dona is 70,000 ton per year and now it has been reduced to about 28000 ton yearly. Stone mine extracts have high amounts of silver, zinc sulfur, sodium carbonate and pyrite. In production process, lead is separated from gold, silver, zinc and iron but much lead is deposited in waste. Figure 1 shows the situation of the Sorb Dona mine rather than other stations. The Vali Abad Station is situated at 67 km of Chalus River; Pole Zoghal Station at 22 km of Chalus River; and Masab Station at 1 kilometer of the Caspian Sea. These stations are same with hydrometery stations.

### METHODOLOGY

Sediment samples and suspended particle were collected pb three selected stations, located on the Chalus River: Vali Abad, Polezoghal and Masab. Adsorption of four metal ions such as Cu, Zn and Fe were surveyed. Adsorbents were suspended particles and bottom sediments. In this experiment, sediment concentration was tested in a range of 1000 to 11000 mg/L. Sediment samples were each dispersed in original river water and blank sample for station. Determined volumes of heavy metal ions solution were added to reaction beaker in the range of 5 - 15 ppm. Selection of this range was according to previous observation and laboratory results of

**Table 1.** Sediment and suspended particle size (%) by station.

| Station | 0.42 < (mm) | 0.42 > (mm) | 0.075 > (mm) | 0.075 < (mm) |
|---|---|---|---|---|
| Vali abad | 44 | 56 | 27 | 73 |
| Polezoghal | 22 | 78 | 62 | 38 |
| Masab | 3 | 97 | 83 | 17 |

**Table 2.** Total organic carbon (TOC) in mg/l.

| Station name | Total organic carbon |
|---|---|
| Valiabad | 11.12 |
| Polezoghal | 13.94 |
| Masab | 23 |

wastewater effluent Sorb Dona mine for peak times. The beakers were shaken by Jar Test apparatus at similar temperatures for two contact times for 30 and 60 min and the solid phase was separated by filtration through a 0.075 mm membrane filter, according to sediment particle size determination (Table 1). The amount of adsorbed metal onto the solid phase was calculated by the difference between the amount of metal added and the final soluble concentration. The filtrates were analyzed for heavy metal ions concentrations using the conventional method of flame atomic absorption spectrometery (model: GBC 903).

In addition, we have measured Total Organic Carbon (TOC) amount in each water station. TOC was measured by combustion-infrared method. In this method the sample is homogenized and diluted as necessary and a micro portion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The water is vaporized and the organic carbon is oxidized to $CO_2$ and $H_2O$. The $CO_2$ from oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a non dispersive infrared analyzer. For evaluation of the capacity of adsorption, an experiment was done within the range of concentration of 1000 to 11000 mg/l.

This range is on base dates of hydrometery stations. The result of analysis of Total Organic Carbon (TOC) showed that the capacity (TOC) increased from the Valiabad Station to the Masab Station. These results are shown in Table 2. The results of physical and chemical water quality are shown in Table 3. This analysis was done, besides adsorption analysis.

## RESULTS

According to the last analysis, the maximum concentration of Pb in the Dona Sorb mine wastewater is equal to 12.7 mg/l and concentrations of Cu, Zn and Fe were around 3.7 mg/l. But we consider concentration of 15 mg/l for Pb and 5 mg/l for Cu, Zn and Fe until the highest adsorption capacity was determined (The Environment Protection Administration of Mazandaran, 2005 - 2009).

After addition of standard metals to river water and blank and before addition of suspended particle and sediment to samples, we calculate real concentration metals of Pb total, Cu total, Zn total and Fe total. Also according to the last analysis, range of suspended particle and sediment in Chalus River is around 1000 - 11000 mg/l and selected contact time was according to water velocity; and selected twice for 30 and 60 min was vision adsorption behavior (The Regional Water Company of Mazandaran, 1980 - 2009). The following graphs show adsorption capacity of each metal. In these graphs, horizontal axis is station axis and vertical axis is concentration of metals and adsorption capacity.

### Adsorption capacity of Pb

Generally, results point out that the concentration of particles is proportional to its adsorption capacity, however there were exceptions. The adsorptive capacity of sediment, v, is the adsorption value of heavy metal ions on suspended particles for a unit of water volume. Figure 2 shows the removal capacity of Pb by suspended particles and sediment arrangement that is equal to 1000 to 11000 mg/l concentrations.

### Adsorption capacity of Cu

Figure 3 shows the results of removal capacity of Cu with 5 mg/l concentration by suspended particles and sediment from 1000 to 11000 mg/l concentrations.

### Adsorption capacity of Zn

Figure 4 shows the results of adsorption capacity of Zn with 5 mg/l concentration by suspended particles and sediment from 1000 to 11000 mg/l concentrations.

### Adsorption capacity of Fe

Figure 5 shows the results of removal capacity of Fe with 5 mg/l concentration by suspended particles and sediment from 1000 to 11000 mg/l concentration.

## DISCUSSION

This research has studied the adsorption capacity of the heavy metal ions Cd, Cu, Zn, Pb on Chalus River bottom sediments and suspended particles. We conclude by using the above figures and tables to draw the following description:

1) With a change of contact time from 30 to 60 min, the

**Table 3.** The results water quality of the Chalus river.

| Sampling place | pH | TSS (mg/L) | TDS (mg/L) | TSS mg/L | EC*$10^{-6}$ (µs/cm ) | Turbidity (NTU) | $Cl^-$ (mg/L ) | N- $NO_3$ (mg/L) | N- $NO_2^-$ (mg/L) | $Po_4$ (mg/L) | BOD (mg/L) | COD (mg/L) | Dissolved Oxygen (mg/L) | Temp. (°C) | N-NH3 (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Offspring | 7.19 | 32 | 164 | 32 | 238 | 29 | 11.36 | 1.29 | 0.003 | 0.004 | 1.5 | 4 | 7.8 | 6.5 | 0.05 |
| Valiabad | 7.49 | 180 | 292 | 180 | 424 | 201 | 12.78 | 0.84 | 0.001 | 0.003 | 3.5 | 8 | 7.3 | 11 | 0.044 |
| Dozdbon | 7.58 | 189 | 290 | 189 | 416 | 220 | 14.2 | 0.82 | 0.001 | 0.01 | 4.9 | 9.5 | 7.16 | 12.5 | 0.039 |
| Polezoghal | 7.67 | 245 | 268 | 245 | 387 | 360 | 12.78 | 0.93 | 0.002 | 0.005 | 5.4 | 12 | 7.68 | 14 | 0.039 |
| Masab | 7.74 | 251 | 266 | 251 | 383 | 365 | 12.78 | 0.94 | 0.002 | 0.007 | 7 | 16.5 | 7.68 | 14 | 0.041 |
| Offspring | 7.80 | 273 | 264 | 273 | 383 | 370 | 15.62 | 0.96 | 0.002 | 0.006 | 2.5 | 6 | 7.6 | 14 | 0.044 |
| Valiabad | 7.65 | 9 | 226 | 9 | 327 | 4 | 5.68 | 0.36 | 0.002 | 0.003 | 3.8 | 8.5 | 7.04 | 15.5 | 0.046 |
| Dozdbon | 7.75 | 16 | 664 | 16 | 892 | 11 | 42.6 | 0.56 | 0.003 | 0.004 | 9 | 22 | 6.84 | 16.5 | 0.055 |
| Polezoghal | 7.60 | 21 | 572 | 21 | 818 | 23 | 34.08 | 1.51 | 0.009 | 0.03 | 3.8 | 12 | 6.16 | 17 | 0.078 |
| Masab | 7.68 | 110 | 450 | 110 | 647 | 416 | 36.92 | 0.92 | 0.003 | 0.006 | 6.5 | 16 | 6.08 | 18.5 | 0.059 |
| Offspring | 7.15 | 12 | 226 | 12 | 327 | 3.2 | 18.46 | 0.129 | 0.001 | trace | 1 | 2.5 | 8.87 | 6.5 | 0.022 |
| Valiabad | 7.80 | 26 | 422 | 26 | 610 | 22 | 42.6 | 0.599 | 0.001 | 0.001 | 0.3 | 1.9 | 8.49 | 15.5 | 0.036 |
| Dozdbon | 7.85 | 75 | 434 | 75 | 621 | 62 | 28.4 | 1.206 | 0.02 | 0.041 | 8 | 26 | 7.8 | 16 | 0.285 |
| Polezoghal | 7.75 | 115 | 452 | 115 | 647 | 319 | 28.4 | 1.001 | 0.003 | 0.002 | 4.5 | 15.3 | 8.17 | 18.5 | 0.042 |
| Masab | 7.20 | 15 | 121 | 15 | 312 | 20 | 17 | 0.18 | 0.001 | 0.001 | 7 | 16.7 | 8.56 | 14.5 | 0.019 |

Temp., Temperature; COD, chemically dissolved oxygen; BOD, biologically dissolved oxygen; DO, dissolved oxygen.

average adsorption capacity of Pb ion for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 28.31, 43.33, 45.28 and 84.38%. The purpose of the percentage difference in amount of initial residual ion is seen in sample solution.

2) In 30 min contact time, the average adsorption capacity of Cu ion for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 32.44, 33.1, 44.8 8 and 85.38%. In 60 min contact time, the average adsorption capacity of Cu ions for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 35.18, 66.01, 68.61 and 85.22%, respectively.

3) In 30 min contact time, average adsorption capacity of Zn ions for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 2.8, 6.93, 4.8 and 17.93 percent, respectively. In 60 min contact time, the efficiency of removal of Zn ions for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to1.2, 7,96, 8.9 and 32.4%, respectively.

4) In 30 min contact time, average adsorption capacity of Fe ions for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 0.8, 9.43, 72.8 and 87.73%, respectively. In 60 min contact time, average adsorption capacity of Fe ions arranged for 1000, 3000, 7000 and 11000 mg/l of suspended particle and sediment is equal to 0.27, 49,86, 69.06 and 93.74 mg/l, respectively.

5) According to the figures given, increase in adsorption capacity leads to decrease in suspended particle, sediment diameter and in the blank sample, too.

6) With increase in TOC in Masab, the adsorption capacity increases and this is because of carbon material bonds.

7) Behavior graphs changed in Pol Zoghal samples and that indicates the interaction point; this is because inflow sanitary wastewater and inflow wastewater fish-growing fields and chloride, nitrite and nitrate are more than other stations.

8) Increase in suspended particle and sediment increases the adsorption capacity of Fe ion and also the compound, Fe and chloride.

9) With increase in DO from Vali Abad to Masab, it shows that the river has turbulent flow.

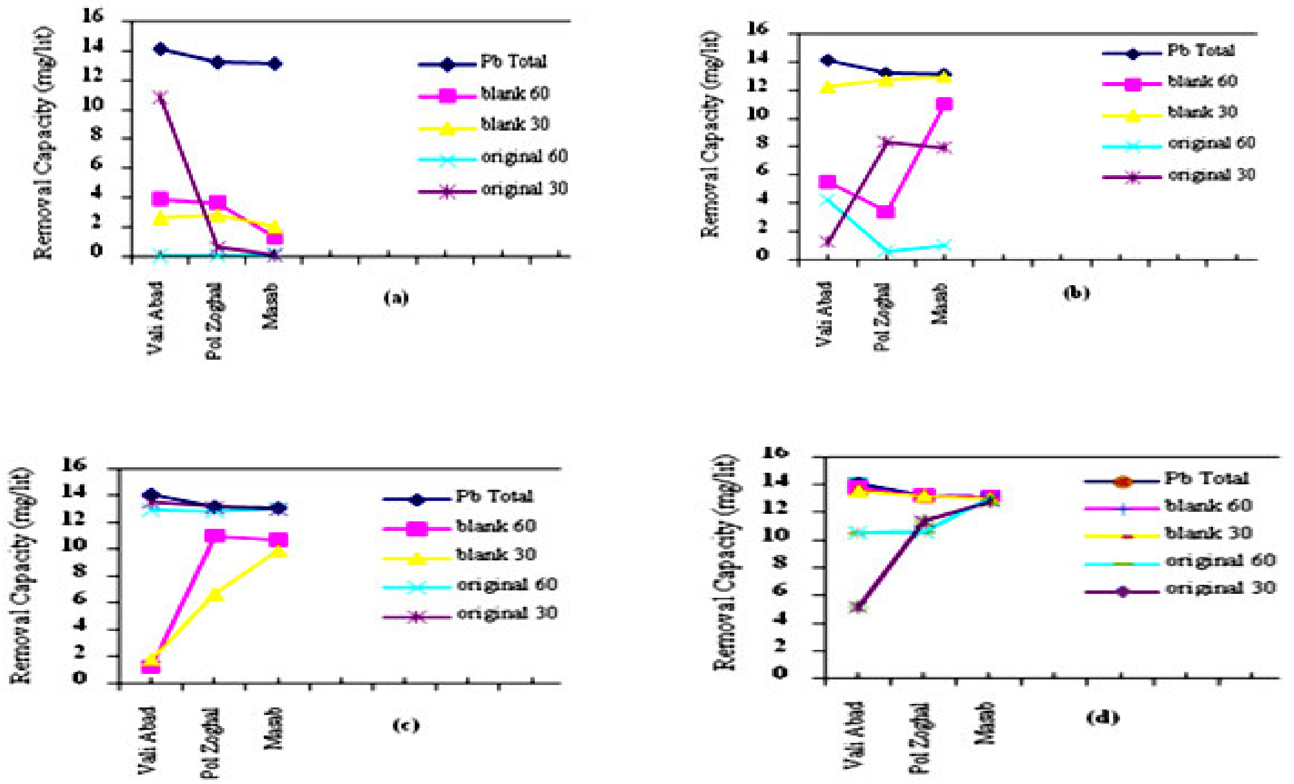


**Figure 2.** Adsorption capacity of Pb by suspended particles and sediments concentrations: a) 1000 mg/l, b) 3000 mg/l, c) 7000 mg/l and d) 11000 mg/l.

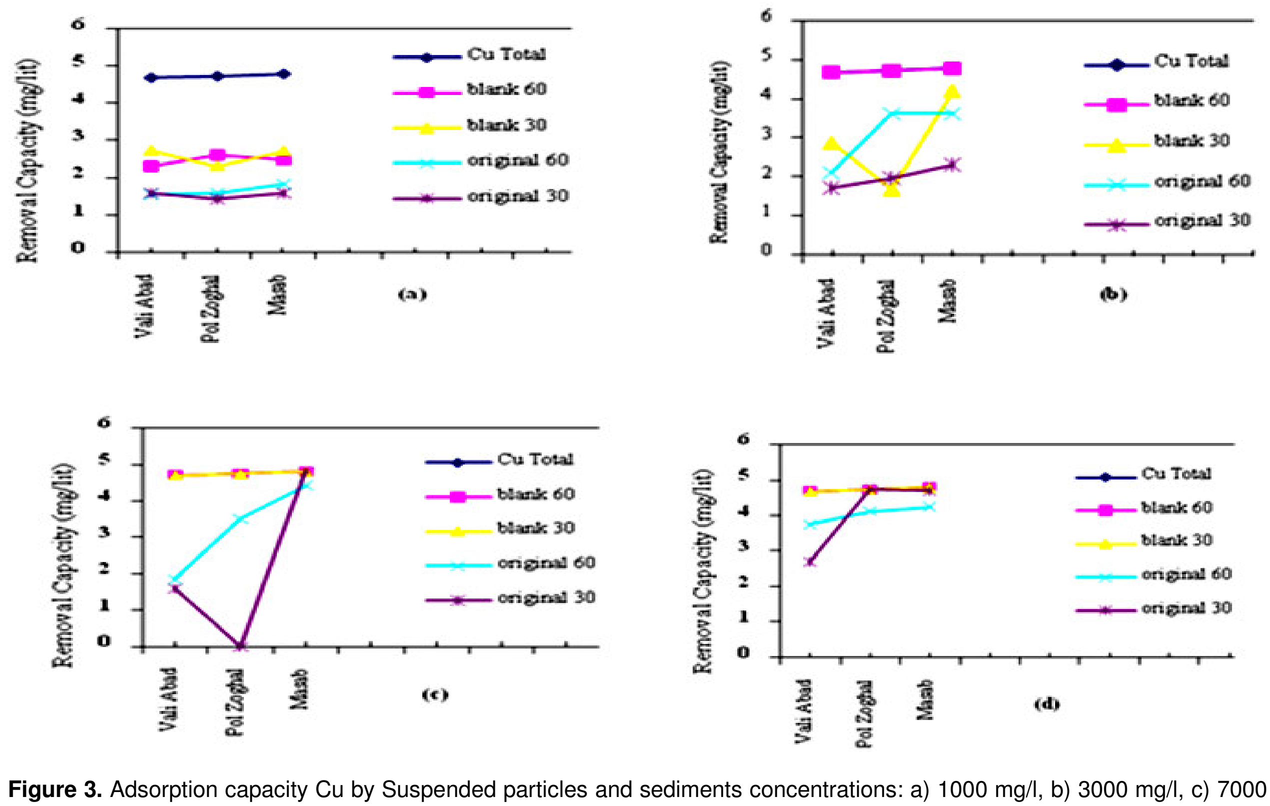


**Figure 3.** Adsorption capacity Cu by Suspended particles and sediments concentrations: a) 1000 mg/l, b) 3000 mg/l, c) 7000 mg/l and d) 11000 mg/l.

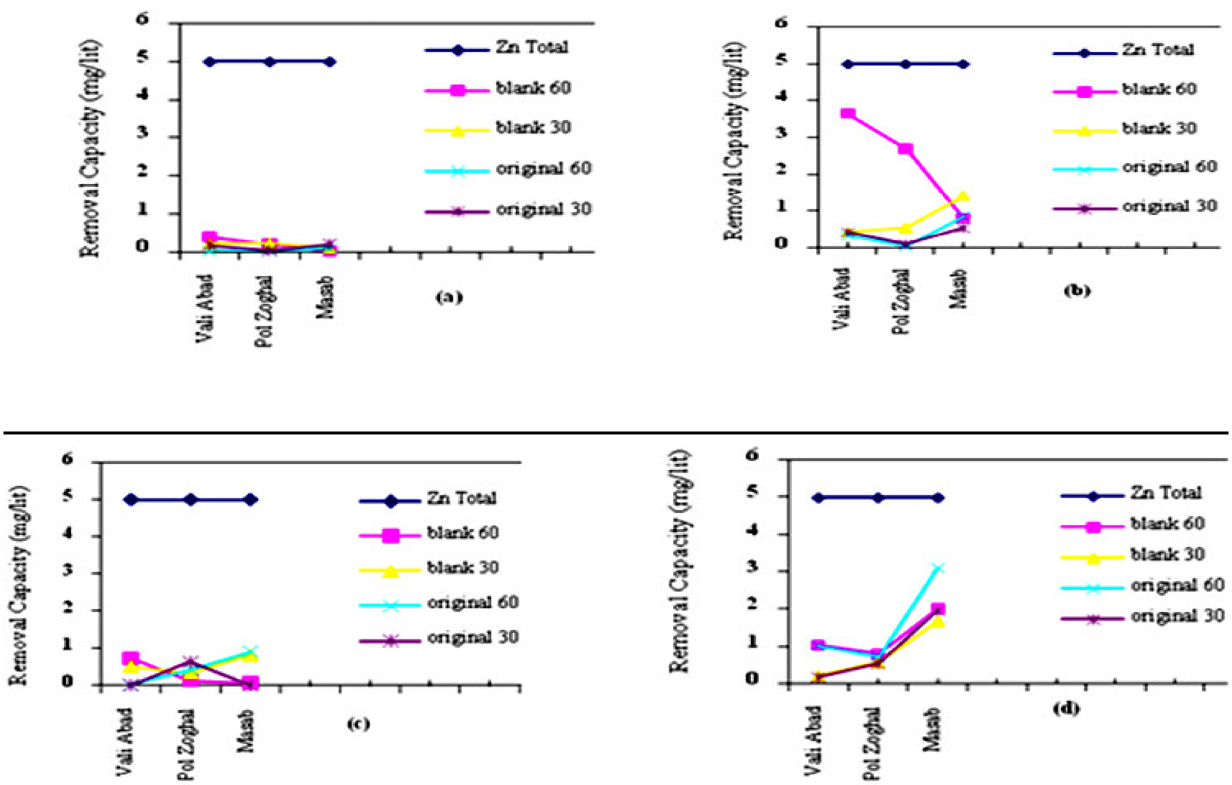


**Figure 4.** Adsorption capacity of Zn by suspended particles and sediments concentrations: a) 1000 mg/l, b) 3000 mg/l, c) 7000 mg/l and d) 11000 mg/l.

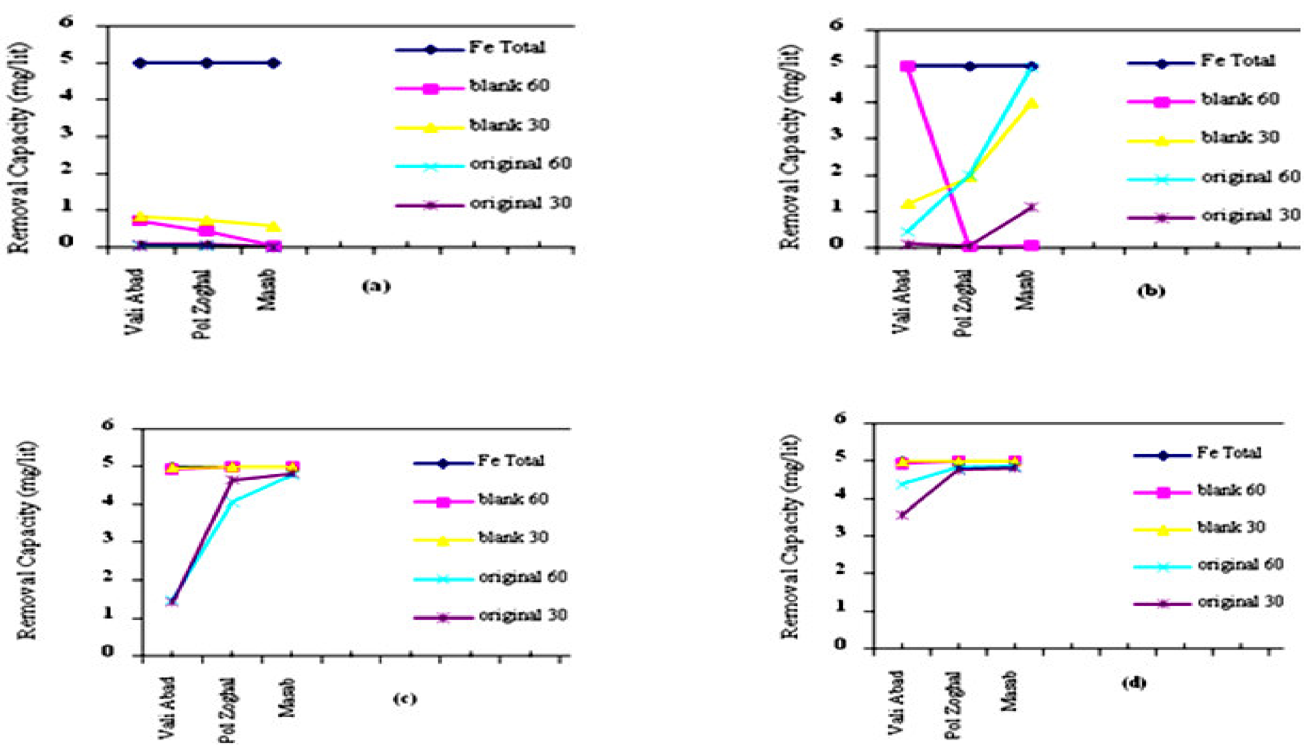


**Figure 5.** Adsorption capacity of Fe by suspended particles and sediments concentrations: a) 1000 mg/l, b) 3000 mg/l , c) 7000 mg/l and d) 11000 mg/l.

10) With the v calculation and situation data in adsorption equations, we see that adsorptive capacity follows the Freundlich adsorption isotherm.

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