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RESEARCH ARTICLE

REMOVAL OF HEAVY METALS FROM CHEMICAL INDUSTRIAL WASTEWATER USING AGRO BASED BIO-SORBENTS

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ABSTRACT

Textile industries uses a numerous amount of heavy metals in different processes and significant losses during the process and are discharged in the effluent. With the new advancement and development in world, severe problems including the waste water containing hazardous heavy metals deteriorating the ground water. Only about 8% of industrial waste water is treated before discharge. Use of bio-sorbents for heavy metal removal from wastewater is a cost-effective method due to their nature of agricultural waste. This study use to remove the heavy metals (Cr, Pb and Ni) from wastewater through agriculture based bio-sorbents, rice husk and eggshells of hen. The pretreatment applied to rice husk by treating with formaldehyde for removal of chromium. The pretreatment for egg shells is calcination at 800° C for 2 hours. Bio-sorbents have applied in varied doses like 1g, 2g at temperature between 25°C and 28°C. The maximum efficiency of rice husk is for chromium that is 95% for synthetic solution and 100% for Nickle removal by applying 1g dose to wastewater. The removal efficiency of eggshells is 61% for synthetic solution of lead (Pb). Therefore, it is concluded rice husk is more efficient as bio-sorbent as compared to eggshells, but removal efficiency of rice husk decreases with increasing doze of rice husk

KEYWORDS

effluent treatment, bio-sorbents, heavy metals, Industrial wastewater

1. INTRODUCTION

The world's population is growing and concentrating in urban areas. This trend is predominant in developing countries, where more than 2.1 billion people are expected to increase in cities by 2030 [1]. These resources produce around 330 km³ of municipal wastewater in the world every year that would be sufficient to irrigate millions of hectares of land. The heavy metals present in wastewater effect the bones, kidneys, liver, lungs and brain when injected in the body through a number of path ways [2]. When toxic metals are exposed to natural eco-system, metal ions such as lead, chromium, mercury and cadmium accumulate in body through direct intake or from food chains [3].

Heavy metals have capacity to bio-accumulate and remain as long-lasting destructive elements in environment. Heavy metals in ground and surface water is a major environmental concern. Heavy metals (Pb, Zn Cd, Ni, Cr, Cu etc) and metalloids (e.g As) in drinking water have adverse impacts on human health such as skin lesions & cancer, allergies, neurological effect, hyper pigmentation, cardiovascular disease, hypertension, and pulmonary disease [4]. Heavy metal pollution comes in waste streams from industrial sector such as car radiator manufacturing, metal plating, tanneries, mining, painting, and agricultural sources where fungicidal spray and fertilizers are used contain Cr, Cu, Cd, Zn etc. The industrial sector produces harmful heavy metal waste, as a result contaminating water resources and ground resources. For example, chromium is responsible for several serious disorders in animals and plants [5]. Cd is measured as latent carcinogen and associated with the generation of a number of diseases, specifically bone, cardiovascular, nervous, kidney and blood diseases [6]. The contaminated environment with heavy metal poses a serious danger to human beings, animals and plants [7].

Several physio-chemical methods have been used for removal of heavy metal contaminated aqueous streams [8,9]. Conventionally, techniques to remove heavy metals from wastewater include chemical precipitation, membrane filtration, carbon adsorption and ion exchange etc. But these are costly and are not suitable for high heavy metals concentration [10,11]. We require less expensive and effective alternatives that can be easily use and offers less maintenance. Among all the removal techniques, the adsorption technique has gained importance due to its cost effectiveness, high efficiency, availability and handling [12]. Bio-sorbents have appeared to be possible alternatives for removal of heavy metals. Algae, fungi and plants are biomass derived bio-sorbents that are capable of removing metalloids and heavy metals from aqueous solution through biosorption [13]. Biosorption possess several advantages over conventional methods like high efficiency, low cost, minimization of biological and chemical sludge, regeneration of bio-sorbent, possibility of metal recovery and no additional nutrient requirement [14]. Most important task is selection of adsorbent and its efficiency, economics and versatility of process depends on selection of adsorbent [15]. The activated carbon has been used widely in decades due to availability of less choice among adsorbents. Over the years, due to less economical activated charcoal, the focus of world has been shifted to research and development so that to discover alternatives that are cost efficient, versatile to replace commercially available less economical adsorbents, considerably waste materials [16,17].

In recent years, different agricultural wastes have been tested for their heavy metal's removal efficiency from wastewaters. Several agricultural wastes studied for the biosorption efficiencies in recent past include rosewood saw dust, rice husk, maize corn cobs, sugarcane bagasse.

jatropha oil cake etc. [18,19].

Rice husk an agricultural waste studied and proved as good sorbent of many heavy metals, contains 20% silica [20-22]. Rice husk being insoluble in water, structural strength due to high silica content, having good chemical stability, have been used by many researchers for handling heavy metal in ground water and surface water [23]. It would reduce waste disposal cost and also provide sorbent that is low cost and have potential to compete with commercially available techniques. Kumar and Bandyopadhyay worked on removal of Cadmium (cd) by using rice husk treated by sodium carbonate. The fixed bed of pre-treated rice husk with sodium carbonate developed for the cadmium removal. The diameter of column is 2cm and with different ratio of bed depths (10, 20 and 30 cm). Results proved that rice husk is an efficient biomaterial with efficiency and low cost that can be used for removal of heavy metals [24].

The egg shells are material that come out in large quantities as a waste from homes, bakeries, food industries and restaurants and become the part of landfill site [25]. The bakeries and food manufacturing units are biggest sources of egg shells and disposal of eggshells waste is a challenge for the authorities [26]. However, a researcher claimed that the disposal procedures for waste egg shells are 21.1% as animal feed constituents, 26.6% as manure, and 26.3% discarded in municipal landfills, and 15.8% used in other ways [27]. The technique that attracted the attention of research world is utilization of egg shell as bio-sorbent in waste water treatment.

This research study conducted here investigates about the removal of heavy metals (Cr, Pb and Ni) from industrial waste water by using rice husk and eggshells as bio-sorbents. And these two bio-sorbents are compared in terms of efficiency, availability and cost effectiveness.

2. MATERIALS AND METHODS

2.1 Materials

Rice husk was taken from a local unit. Impurities were separated manually. Rice husk contains 75-90 % organic matter such as cellulose, lignin etc. and rest mineral components such as silica, alkalis and trace elements. Presence of high amount of silica makes it a valuable material for use in industrial application.

Eggshells were collected from bakery and hostel mess. The eggshells washed with tap water (several times) and then with distilled water (3 times). It is a low-cost sorbent and easily available. It is easy to Use. Egg shells have relatively high sorption capacity, when comparing with other sorbents that was evaluated as 21–160 mg/g.

Figure 1: Raw Material (a) Raw Rice husk (b) Raw Eggshells

2.2 Wastewater Sampling

Wastewater samples were collected from Captain-PQ Chemicals Industry, Sargodha road, Faisalabad located at latitude 31.471442 and longitude 73.078558. Sampling site is shown in figure 2. The collected samples were reserved in PET Bottles. Samples were collected by Grab sampling technique, the most common form of sampling of flowing water, reliable and easy to do.

According to Environmental Quality Act 1974, standards of heavy metal effluent are shown in Table 1.

Table 1: Environmental Quality Act 1974, standard limits for heavy metal effluent.

Parameters	**Standard value (**mg/l)
Nickel	0.2
Lead	0.1
Chromium	0.2

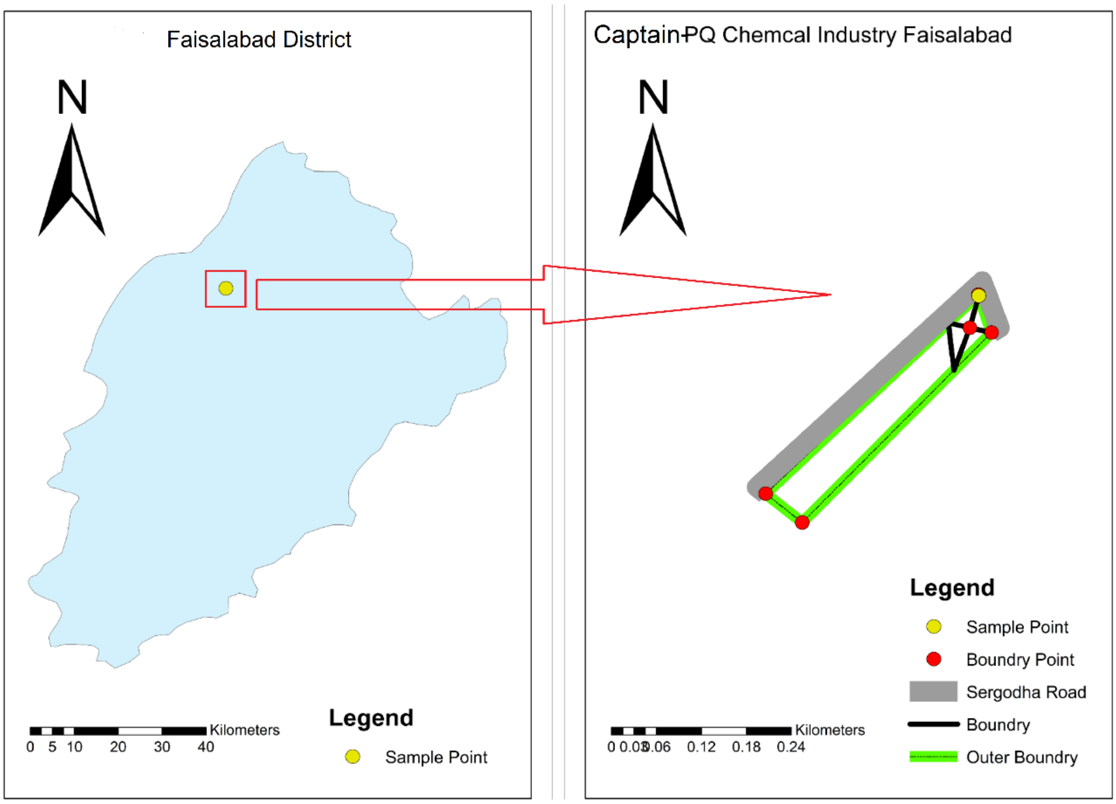


Figure 2: Captain-PQ Chemicals industry (Sampling site)

2.3 Preparation of Synthetic Solutions

Aqueous solution of chromium (Cr), and lead (Pb) were prepared in a 1000 ml volumetric flask. Magnetic stirrer was used to completely dissolve the salts of heavy metals in distilled water. The solution was then made up to 1000 ml and aqueous solution was then diluted with distilled water to obtain the Cr and Pb synthetic solution. AR grade chemicals and distilled water were used for all the analysis. Specifications of Metal salts are shown in Table 2.

Table 2: Specifications of Metal salts and their concentrations used for preparation of synthetic solution

Heavy Metal	Metal Salt used	Purity of Metal Salt (%)	Amount of Metal Salt used (g)	Volume of solution made (mL)	Conc. Of heavy metal in solution (mg/L)
Cr	Chromium nitrate	99	250	1000	1.21
Pb	Lead nitrate	99.5	250	1000	25.46

Figure 3: Prepared Synthetic Solutions of Heavy Metals

2.4 Pre-treatment of rice husk

2.4.1 Preparation of pre-boiled rice husk

The collected rice husk was dried under sun and impurities were separated manually. It was boiled with distilled water for 5 h to make. It free from colored compounds and filtered. The residual material so obtained was dried at 80◦ C in hot air oven for 24 h, and then the. The material was grinded and sieved through the sieves of 30 mesh size. The material was stored in airtight plastic container for further use.

2.4.2 Preparation of Phosphate treated rice husk

Five-gram dried rice husk was treated with 100 ml of 1.0 M K_2HPO_4 for 24 h. The mixture was filtered and washed several times with distilled water to remove the excess phosphate from the treated rice husk. The resultant bio-sorbent was finally dried at 80◦ C for 24 h and preserved at room temperature in a sealed bottle. All the chemicals used were of analytical grade.

2.4.3 Preparation of Formaldehyde treated rice husk

To immobilize the color and water-soluble substances the rice husk was treated with 1% formaldehyde in the ratio of 1:5 (rice husk: formaldehyde, w/v) at room temperature (27±3 ◦C) for 24 h. The rice husk was filtered, washed with distilled water to remove free formaldehyde and dried at 80 ◦C in a hot air oven for 24 h. The resulting material was sieved through the sieves of 30 mesh size. The material was stored in airtight plastic container for further use.

2.5 Pre-treatment of eggshells

2.5.1 Drying and crushing

Washed eggshells were dried at 80⁰ C in hot air oven. Eggshells were crushed and dried in hot air oven again at 60° C. Crushed eggshells were passed through a sieve with mesh 25. And reserved for further processing.

2.5.2 Calcination

Calcinations is the process of subjecting a substance to the action of heat, but without fusion, for the purpose of causing some change in its physical or chemical constitution. Calcination was performed in the muffle furnace at 800°C for 2 h after crushing the dried sample. This fraction was approximately 70% of the total dried sample. The IUPAC defines it as heating to high temperatures in air or oxygen. However, calcination is also used to mean a thermal treatment process in the absence or limited supply of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition.

Figure 4: Pretreated (a) Rice husk (b) Eggshells

2.6 Adsorption Experiments

2.6.1 Treating with Rice husk

Batch experiments were carried out at various bio-sorbent dose (1-2g) at stirring speed of 100rpm for a contact time of 3h. Fifty milliliters of the synthetic solution with initial concentration 1.21mg/l of Cr was treated with 1 g and 2g of bio-sorbent. It was allowed to remain in contact with the bio-sorbent for 3 h. After that the sample is filtered to remove solids present in the sample by using filter paper, glass funnel and Beaker. Similarly following the same procedure two doses (1g and 2 g) of rice husk is applied to fifty milliliters of wastewater.

2.6.2 Treating with Eggshells

For eggshells, two doses of 1.5g and 2.5g of eggshell were applied to 200 ml synthetic solutions of heavy metals (Pb and Cr) at 100 rpm and at temperatures between 25–28°C for 1 hour. After that solutions were filtered to remove solids present in the sample by using filter paper, glass funnel and Beaker. Same procedure is adopted for treating wastewater samples with eggshell. But for wastewater samples natural crushed eggshells (without calcination) are utilized.

2.7 Heavy metal Determination by Atomic Absorption Spectrophotometer

2.7.1 Standards Preparation

Calibrated standards were prepared from the commercially available stock solution (Applichem) in the form of an aqueous solution (1000 ppm). Highly purified de-ionized water was used for the preparation of working standards. All the glass apparatus used throughout the process of analytical work were immersed in 8N HNO3 overnight and washed with several changes of de-ionized water prior to use.

2.7.2 Heavy metal Determination

After treatment with bio-sorbents heavy metals in the samples were determined by using Atomic Absorption Spectrophotometer (Hitachi Polarized Zeeman AAS, Z-8200, Japan) following the conditions described in AOAC (1990). Selected elements included Chromium (Cr), Lead (Pb) and Nickel (Ni). The instrumental operating conditions for the said elements are summarized in Table 3

Table 3: Operational Conditions Employed in the Determination of Heavy Metals by Atomic Absorption Spectrophotometer

Elements	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Burner Head	Flame	Burner Height (mm)	Oxidant gas pressure (kpa)	Fuel gas Pressure (kpa)
Cr	359.3	1.3	7.5	Standard type	Air-C_2H_2	7.5	160	12
Pb	283.3	1.3	7.5	Standard type	Air-C_2H_2	7.5	160	7
Ni	232.0	0.2	10.0	Standard type	Air-C_2H_2	7.5	160	7

Figure 5: Hitachi Polarized Zeeman AAS, Z-8200, Japan

3. RESULTS AND DISCUSSION

The rice husk applied in two doses 1g and 2g to synthetic solutions of chromium and cadmium. By applying 1g dose, rice husk has reduced the concentration of chromium from 1.21 mg/l to 0.06 mg/l. Similarly, by applying 2g dose of rice husk to chromium synthetic solution, the concentration has been reduced from 1.21 mg/l to 0.19mg/l. Concentration of nickel has been removed totally form initial concentration of 0.04 mg/l by applying 1g dose of rice husk to waste water sample and it is reduced to 0.02 mg/l by applying 2g of rice husk.

The chromium concentration in synthetic solution has been reduced from 1.21 mg/l to 0.23 mg/l and 1.21 mg/l to 0.14 mg/l by applying 1.5g and 2.5g dozes of eggshells respectively. Similarly, by applying 1.5g and 2.5g to synthetic solution of Lead, its concentration decreases from 25.46 mg/l to 10.86 mg/l and 9.83 mg/l respectively. The nickel has been removed from 0.04 mg/l to 0.03mg/l by applying 1.5g doze of egg shells and 0.04 mg/l to 0.02mg/l for 2.5g doze of egg shells to wastewater.

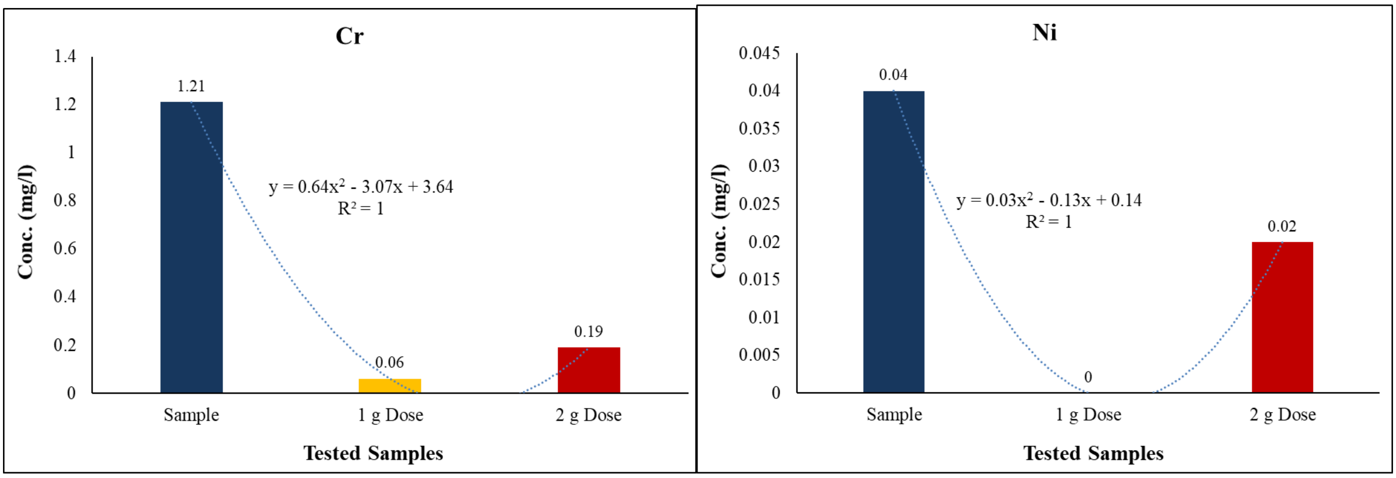
Figure 6(a) shows that rice husk has removed about 95% of chromium concentration from synthetic solution by applying 1 g of rice husk that removed 1.15 mg/l and reduces initial concentration of 1.21 mg/l to 0.06 mg/l. Figure 6 (a) & (b) shows that by increasing the dose of rice husk the removal efficiency decreases, as by applying 2g dose the efficiency decreases by 11% as this dose removed 1.02 mg/l that is 84 %.

Fig 7 shows that absorption efficiency of eggshells increases with the increase in dose, such as by applying 1.5 and 2.5g dose of eggshells the removal efficiency was 81% and 88% respectively for Chromium.

The both bio-sorbents rice husk and eggshells are applied to waste water collected from P.Q Chemical industry for nickel removal. Figure 6(b) shows that the removal efficiency rice husk for nickel removal is 100% for 1g dose and 50% for 2g dose. In case of eggshells Figure 7 (b) shows that removal efficiency of 25% by applying 1.5g dose and 50% for 2g dose.

A previous researcher worked on Removal of Zn, Pb and Cr in Textile Wastewater Using Rice Husk as a Bio-sorbent [28]. It was found that the concentrations of Zn, Pb and Cr were decreased up to 57, 59 and 58 %, respectively. Another researcher studied about Removal of Heavy Metals from Industrial Wastewater Using Rice Husks and found the kinetic removal in batch experiment shows that the net uptake of Pb, Cd, Cu, Zn was 54.3%, 8.24%, 51.4% and 56.7%, respectively [29]. According to a study, the removal of heavy metals using waste eggshell [30]. When calcined eggshell was applied in the treatment of synthetic wastewater containing heavy metals, 40 % removal of Cd as well as above 90% removal of Cr was observed. M. G. a previous researcher has examined Removal of Ni (II) from aqueous solutions using rice husk and concluded that maximum removal of Ni (90.09%) was observed at 100 ppm [31].

These all are the previous studies undertaken to investigate the application of rice husk and eggshells for the removal of heavy metals from wastewater. The results of these studies support the results of present research work.



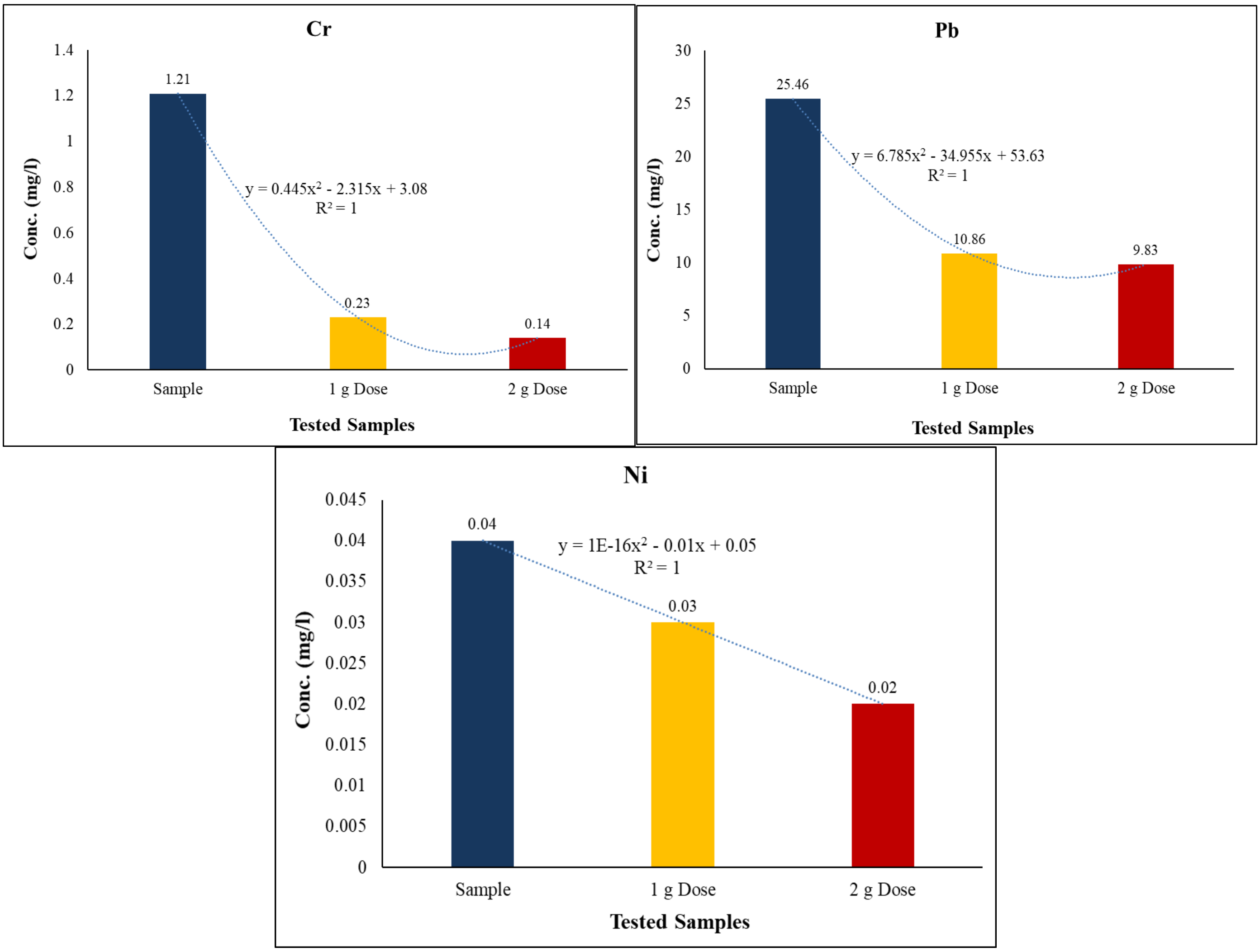


Figure 7: The reduction in heavy metals concentration with varied doses of Eggshells (a) Cr reduction in synthetic solution (b) Pb reduction in synthetic solution (c) Ni reduction in wastewater

4. CONCLUSION

This study was undertaken to examine the adsorption of Chromium, Nickel and Lead on rice husks and eggshells bio-sorbents. Rice husk exhibited the higher potential of removing all the studied heavy metals as compared to eggshells. Adsorption capacity of rice husk decreases in the order of Ni>Cr and for Eggshells adsorption capacity decreases in the order Cr>Pb>Ni. The adsorption was found to be strongly dependent on adsorbent dose, contact time and initial heavy metals concentration. Removal of both Pb and Cr in synthetic solution was much enhanced in the presence of calcined eggshell, however, removal of Ni was rather favorable with natural eggshell. Rice husk is more efficient in removing heavy metals from samples, but with increasing dose its efficiency decreases. On the other hand, eggshells are less effective in removing heavy metals as compared with rice husk, however its removal efficiency increases with increasing dose of eggshells. Another aspect is availability of the both the Bio-sorbents. Rice husk is easily and abundantly available as compared with eggshells.

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