INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 5, Issue 1, January-March 2014: 69-78 www.ijcs.uaic.ro

REMOVAL OF HEAVY METALS FROM WINERY WASTEWATER BY USING NATURAL ADSORBENTS

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Abstract

Winery wastewater compositions are highly variable and differ significantly from season to season. Heavy metals, such as Cd, Pb, Cu, Ni, Zn, Mn and Mg are present in the wastewater. The quantity of heavy metals in winery wastewater can be reduced by an adsorption process with good efficiency. For our comparative adsorption efficiency study, four adsorbents, such as neem leaf, orange peel, coconut husk and saw dust were used. All the adsorbents were sieved through a 0.25mm pore size sieve. Polypropylene bottles with 300mL capacity were filled with 50mL of the winery wastewater and 2g of each adsorbent. The bottles were shaken for 1hour at 180rpm on a rotary shaker at room temperature and after shaking, the samples were filtered and analyzed for their elemental concentrations of heavy metals on AAS, to verify the adsorption capacities of the adsorbents. The results show that saw dust and coconut husk can be used for Cu, for Zn saw dust and orange peel, for Mn coconut husk and orange peel and for Mg orange peel and coconut husk as adsorbents for a partial removal of these metals from the wastewater. The method is simple and cheap and may be applied on a large scale for the removal of heavy metals from industrial wastewaters.

Keywords: *Neem leaf; Orange peel; Coconut husk; Saw dust; Heavy metals; Wastewater.*

Introduction

The worldwide wine production is 261 x 10^5 m^3 of which 69% is from Europe, 18% from America, 5% from Asia, 4% from Africa and 4% from Oceania [1]. In India the wine industry is projected to grow at more than 25% annually in the next decade, making it the fastest growing industry in the country. There are 58 wineries in Maharashtra with investment of 328.97 crores rupees [2]. Wine is one of the functional fermented drinks and has many health benefits [3]. Some wines made from fruits have medicinal value with many additional benefits [4]. The worldwide wine consumption is $228\times10^5 m^3$, distributed by Europe (68%), America (20%), Asia (7%), Africa (3%) and Oceania (2%) [1]. High strength wastewater is generated from the wineries [5]. 10-15 liters water is required for every liter of wine production. Wastewater generated from the winery often contains the equivalent organic load of a city of almost 2,000 people [6]. Winery wastewater compositions are highly variable which depends on the raw materials used [7]. Winery wastewater contains organic compounds, nitrates and phosphates [8]. All the quality and quantity of winery waste differs significantly from season to season.

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During the vintage season two-third of a winery wastewater is generated and during this period the highest organic contamination occurs than the non vintage period. Each season period generates different types of wastes and qualities of wastewaters and hence should be treated separately.

Heavy metals like Cadmium (Cd), Lead (Pb), Copper (Cu), Nickel (Ni), Zinc (Zn), Manganese (Mn) and Magnesium (Mg) are present in the wastewater generated from the wineries [9, 10]. The important toxic metals like Cd, Zn, Ni, and Pb find their way to the water bodies through wastewater [11-13]. These toxic metals pollute the local water and soil environment. Large volume of winery wastewater is disposed by releasing it in grape fields. The over-irrigation at the time of disposal in soil causes environmental impacts such as leaching of heavy metals from the soil. When winery wastewater is disposed into the soil, long term hazard to the environment is encountered. Accumulation of heavy metals in soils can reduce productivity and growth of plants and affect the structure of soil [14]. Heavy metals are toxic to aquatic organisms and cannot be metabolized and hence bio-accumulated in animal body, biomagnified through the food chain and finally get passed up to human being [15]. The contamination of the environment with toxic metals has become a worldwide problem affecting crop yields, soil biomass sustainability and water quality. In the last few decades, research groups have predicted that certain chemical pollutants such as toxic metals may remain in the environment for a long period and can eventually accumulate to levels that could harm humans [16-19].

Heavy metals concentrations in wastewater can be effectively reduced by adsorption on the surfaces of finely divided adsorbents. An adsorption is a process in which dissolved metal is attached to the surface of adsorbent particle. Cost is an important parameter for comparing the sorbent materials [20-23]. Various low cost natural adsorbents have been used for the removal of heavy metals. They include peanut hull [24], teak leaf [25], neem leaf [26], orange peel [27], coconut husk [28] and saw dust [29]. These compounds contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption [30].

Aim of this work was to study the adsorption efficiencies of natural adsorbents like neem leaf, orange peel, coconut husk and saw dust for heavy metals like Cd, Pb, Cu, Ni, Zn, Mn, and Mg from the winery wastewater.

Material and methods

Most of the winery industries in Maharashtra state of India are situated in Nasik district. In this district most of the wastewater is discharged or disposed in landfills, ponds, lagoons, streams and rivers. Two different types of samples were collected for the study, one from point source and other from non-point source. Wastewaters discharged directly from winery industries are collected as point source samples. Non-point source samples were collected from the ponds in which the effluents discharged from winery industries were stored. Winery wastewater composition is highly variable and the quality and quantity of winery wastes differs significantly from season to season. Winery wastes can be divided into two season wastes-vintage and non-vintage [6]. In India, the vintage season begins in February and lasts until May and the non-vintage season involves the period from early October to the end of January. Therefore the sampling of winery and pond wastewater was done in both the seasons i.e. vintage and non-vintage season.

All the samples were collected in polypropylene bottles and stored in a refrigerator (4°C) until the analysis was done. Samples were analyzed for the elemental compositions of heavy metals like Cd, Pb, Ni, Cu, Zn, Mn, and Mg from wastewater prior to adsorption study. It provides the valuable data for the initial heavy metal concentrations which was compared with the heavy metal concentrations after adsorption treatment. The elemental concentrations of heavy metals were determined with flame atomic absorption spectrophotometer i.e. AAS (Make: Thermo Scientific Inc., U.K. and Model: Solar S series). The AAS operating conditions and detection limits for the analysis of metals under study are presented in Table 1.

Table 1. Operational parameters and detection limits of metals under study for AAS analysis

Metal	Source Flame	Flow rate L/min	Lamp Current %	Wavelength nm	Band pass nm	Detection Limit ppm
Cd	Air-Acetylene	1.2	50	228.8	0.5	0.013
Pb	Air-Acetylene	1.1	75	217.0	0.5	0.070
Ni	Air-Acetylene	0.9	75	232.0	0.2	0.050
Cu	Air-Acetylene	1.1	75	324.8	0.5	0.033
Zn	Air-Acetylene	1.2	75	213.9	0.2	0.010
Mn	Air-Acetylene	1.0	75	279.5	0.2	0.020
Mg	Air-Acetylene	1.1	75	285.2	0.5	0.003

For the adsorption studies four natural adsorbents such as neem leaf, orange peel, coconut husk and saw dust were used. All the adsorbents were dried in an oven for 24hours at 110°C. Orange peel and coconut husk were chopped into small pieces and pulverized to get the fine powder and then used as adsorbent. Neem leaf was powdered and used as adsorbent. Saw dust was used as such. All the adsorbents were sieved off from the 0.25mm pore size sieve. The adsorbents were washed and cleaned with distilled water. They were again dried in an oven at 110°C for 24hours to remove the adsorbed moisture.

The experiments were carried out by the batch method for the analysis of heavy metals from the winery wastewater. The polypropylene bottles with 300mL capacity were filled with 50mL of the wastewater sample and 2g of each adsorbent. To get the maximum adsorption of heavy metals the adsorbents were allowed to intimately mix with the winery wastewater [31]. The bottles were shaken for 1 hour at 180rpm on rotary shaker (Make: Steelmate Novatech, India and Model: Tabletop) at room temperature. After shaking each sample with different adsorbents the samples were filtered through Whatman filter paper No. 41 and the filtrates were collected in clean polypropylene bottles. Few drops of 1N nitric acid were added to it, and stored in a refrigerator (4°C) until the metal analysis. The metal concentrations were determined on flame atomic absorption spectrophotometer (AAS) and the results were expressed as averages of triplicate analyses.

Result and discussion

Wastewater discharged outside the winery industry may cause harmful effects to the environment due to presence of heavy metals like Cd, Pb, Cu, Ni, Zn, Mn and Mg. Therefore, it is essential to know the total available concentration of these heavy metals in the winery wastewater before the adsorption study. The adsorption process is superior to many other methods in lowering the concentrations of heavy metals by virtue of its low cost and simplicity of design. Leaves and various parts of trees are very versatile natural chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectin and lignin present in the cell wall and chlorophyll, carotene, anthocyanins and tannin in leaves are the most important sorption sites. In this study four different adsorbents were used such as neem leaf, orange peel, coconut husk and saw dust for removal of heavy metals from winery wastewater samples. The wastewaters collected in vintage and non-vintage seasons were analyzed for the elemental concentrations of heavy metals. It was observed that the three metals viz. Cd, Pb and Ni were not detected in all the winery and pond wastewater samples during vintage as well as non-vintage seasons. The analytical data obtained for other four metals viz. Cu, Zn, Mn and Mg was analyzed statistically. The two sample unpaired t-test was used for the comparison of average concentrations of metals before and after adsorption for the various adsorbents. A significance level of 0.05 for t-test was applied to the adsorption results obtained to know that whether the adsorption of heavy metal on a particular adsorbent was significant or not.

Table 2 shows the results of estimation of adsorption efficiencies of various adsorbents for heavy metals from winery wastewater (www) for vintage season.

Table 2. Adsorption of Heavy metals from winery wastewater (www) during vintage season (n = 3)

Heavy Metal	Adsorbent	Vintage Season (WWW)		% Adsorption Efficiency	p value
		Before Treatment (ppm)	After Treatment (ppm)		
Cu	Neem leaf	0.0187±0.002	0.0157±0.006	16.04	0.22873
	Orange peel		0.0153±0.001	18.18	0.02898
	Coconut husk		0.0124±0.001	33.68	0.00408
	Saw dust		0.0161±0.002	13.90	0.09328
Zn	Neem leaf	4.8483±0.019	2.6073±0.123	46.22	0.00000
	Orange peel		3.3519±0.143	30.26	0.00003
	Coconut husk		3.8220±0.123	21.16	0.00007
	Saw dust		3.4052±1.003	29.76	0.03368
Mn	Neem leaf	0.3054±0.009	0.2014±0.001	34.05	0.00002
	Orange peel		0.2571±0.025	15.81	0.01728
	Coconut husk		0.2153±0.017	29.50	0.00066
	Saw dust		0.2510±0.030	17.81	0.01981
Mg	Neem leaf	25.2630±1.054	20.1512±0.172	20.23	0.00058
	Orange peel		13.2610±0.009	47.50	0.00002
	Coconut husk		15.2312±0.932	39.70	0.00012
	Saw dust		15.1127±0.943	40.17	0.00012

The results indicate that adsorption of Cu was significant on orange peel and coconut husk with adsorption efficiencies of 18.18 and 33.68 % respectively.

Table 3. Adsorption of Heavy metals from winery wastewater (www) during non-vintage season (n = 3)

Heavy Metal	Adsorbent	Non-Vintage Season (WWW)		% Adsorption Efficiency	p value
		Before Treatment (ppm)	After Treatment (ppm)		
Cu	Neem leaf	0.1505±0.009	0.1179±0.016	21.66	0.01828
	Orange peel		0.1003±0.002	33.35	0.00035
	Coconut husk		0.0954±0.005	36.61	0.00038
	Saw dust		0.0843±0.005	43.98	0.00018
Zn	Neem leaf	2.7313±0.255	2.3755±0.021	13.02	0.03683
	Orange peel		2.4118±1.260	11.69	0.34452
	Coconut husk		2.1089±0.010	22.78	0.00672
	Saw dust		1.6518±0.081	39.52	0.00110
Mn	Neem leaf	0.2393±0.055	0.2176±0.009	9.06	0.26851
	Orange peel		0.1629±0.005	31.92	0.03734
	Coconut husk		0.2075±0.097	13.28	0.32362
	Saw dust		0.2215±0.030	7.43	0.32421
Mg	Neem leaf	24.3233±0.968	23.2228±0.988	4.52	0.12012
	Orange peel		14.8901±3.183	38.78	0.00399
	Coconut husk		15.1619±2.679	37.66	0.00254
	Saw dust		14.9901±4.145	38.37	0.00957

The adsorption of Zn was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 46.22, 30.26, 21.16 and 29.76% respectively. The adsorption of Mn was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 34.05, 15.81, 30.81 and 17.81% respectively.

The adsorption of Mg was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 20.23, 47.50, 39.70 and 40.17% respectively. Coconut husk is agricultural wastes and used as metal adsorbent [32]. Table 3 shows the results of estimation of adsorption efficiencies of various adsorbents for heavy metals from winery wastewater (www) for non-vintage season.

The results indicate that adsorption of Cu was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 21.66, 33.35, 36.61 and 43.98% respectively. The adsorption of Zn was significant on neem leaf, coconut husk and saw dust with adsorption efficiencies of 13.02, 22.78 and 39.52% respectively. The adsorption of Mn was significant on only orange peel with adsorption efficiency of 31.92%. The adsorption of Mg was significant on orange peel, coconut husk and saw dust with adsorption efficiencies of 38.78, 37.66 and 38.37% respectively. Orange peel and sawdust are used as adsorbents to remove heavy metals from aqueous solutions [33]. Table 4 shows the results of estimation of adsorption efficiencies of various adsorbents for heavy metals from pond wastewater (pww) for vintage season.

Table 4. Adsorption of Heavy metals from pond wastewater (pww) during vintage season (n=3)

Heavy Metal	**Adsorbent**	**Vintage Season (PWW)**		**% Adsorption Efficiency**	**p value**
		Before Treatment (ppm)	After Treatment (ppm)		
Cu	Neem leaf	0.0765±0.011	0.0597±0.002	21.96	0.03008
	Orange peel		0.0609±0.008	20.39	0.05896
	Coconut husk		0.0592±0.005	22.61	0.03411
	Saw dust		0.0588±0.008	23.13	0.04363
Zn	Neem leaf	3.4514±0.021	2.6012±0.086	24.63	0.00004
	Orange peel		2.4160±0.962	29.99	0.06790
	Coconut husk		3.2808±0.010	33.91	0.00011
	Saw dust		2.2208±0.009	35.65	0.00000
Mn	Neem leaf	0.3526±0.009	0.2917±0.001	17.27	0.00016
	Orange peel		0.2472±0.040	29.89	0.00561
	Coconut husk		0.2014±0.100	42.88	0.02976
	Saw dust		0.2631±0.038	25.38	0.00827
Mg	Neem leaf	25.794±1.110	20.5107±0.019	20.48	0.00059
	Orange peel		14.8550±0.865	42.40	0.00009
	Coconut husk		13.5837±0.010	47.33	0.00002
	Saw dust		15.1712±2.030	41.18	0.00068

The results indicate that adsorption of Cu was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 21.96, 20.39, 22.61 and 23.13% respectively. The adsorption of Zn was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 24.63, 29.99, 33.91 and 35.65% respectively. The adsorption of Mn was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 17.27, 29.89, 42.88 and 5.38% respectively. Azadirachta indica (neem) leaf powder can be used as an adsorbent for the removal of heavy metals from aqueous solutions [34]. Neem leaves can be successfully used for the removal of toxic heavy metal ions from synthetic waste water samples [35]. The adsorption of Mg was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 20.48, 42.40, 47.33 and 41.18% respectively. Table 5 shows the results of estimation of adsorption efficiencies of various adsorbents for heavy metals from pond wastewater (pww) for non-vintage season. The results indicate that adsorption of Cu was significant on neem leaf, coconut husk and saw dust with adsorption efficiencies of 32.94, 25.88 and 44.70% respectively. The adsorption of Zn was significant on neem leaf, orange peel, coconut husk and saw dust with adsorption efficiencies of 43.53, 33.85, 40.04 & 41.06 % respectively. The adsorption of Mn was significant on orange peel, coconut husk and saw dust with adsorption efficiencies of 32.93, 40.48 and 25.93% respectively. The adsorption of Mg was significant on orange peel, coconut husk and saw dust with adsorption efficiencies of 43.74, 40.20, 39.70 and 37.39.17% respectively.

Table 5. Adsorption of heavy metals from pond wastewater (pww) during non-vintage season (n = 3)

Heavy Metal	Adsorbent	Non-Vintage Season (PWW)		% Adsorption Efficiency	p value
		Before Treatment (ppm)	After Treatment (ppm)		
Cu	Neem leaf	0.0085±0.001	0.0057±0.001	32.94	0.01328
	Orange peel		0.0074±0.001	12.94	0.12458
	Coconut husk		0.0063±0.001	25.88	0.02720
	Saw dust		0.0047±0.001	44.70	0.00482
Zn	Neem leaf	3.5757±1.000	2.0190±0.001	43.53	0.02715
	Orange peel		2.3653±0.603	33.85	0.07352
	Coconut husk		2.1437±0.009	40.04	0.03410
	Saw dust		2.1075±0.543	41.06	0.04457
Mn	Neem leaf	0.3401±0.009	0.3107±0.050	8.64	0.18645
	Orange peel		0.2281±0.020	32.93	0.00045
	Coconut husk		0.2024±0.098	40.48	0.03624
	Saw dust		0.2519±0.020	25.93	0.00112
Mg	Neem leaf	25.2620±0.744	23.1712±1.754	8.27	0.06507
	Orange peel		14.2108±0.357	43.74	0.00001
	Coconut husk		15.1051±1.796	40.20	0.00041
	Saw dust		15.8151±2.525	37.39	0.00170

Figure 1 shows the comparison of adsorption efficiencies of various adsorbents for heavy metals from winery wastewater (www) for vintage season.

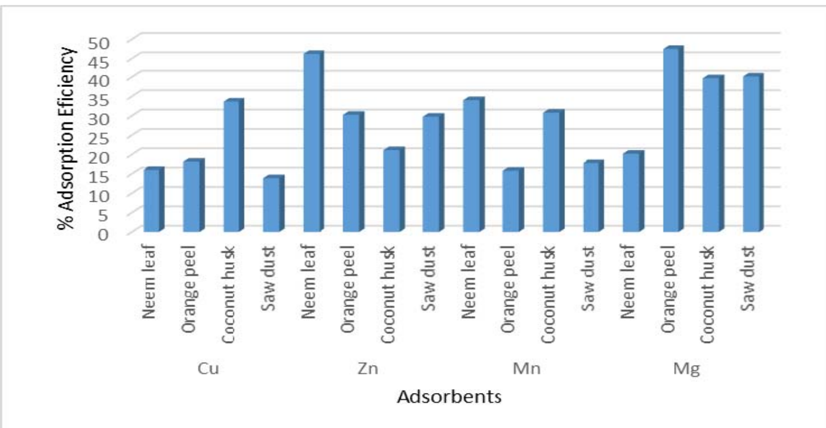

Fig. 1. Adsorption efficiencies of heavy metals for various adsorbents from winery wastewater (www) during vintage season

The results for Cu indicates that coconut husk shows highest while saw dust shows lowest adsorption efficiency and neem leaf and orange peel shows intermediate values. For Zn Neem leaf shows highest adsorption efficiency followed by orange peel and saw dust. Coconut husk indicates lowest efficiency for adsorption of Zn. For Mn coconut husk is the most efficient adsorbent among the adsorbents under study while orange peel is the least efficient one. For Mg Orange peel is the most efficient adsorbent and neem leaf is the least efficient adsorbent among the used adsorbents.

Figure 2 indicates the results of adsorption of heavy metals on various adsorbents under study from winery wastewater for non-vintage season.

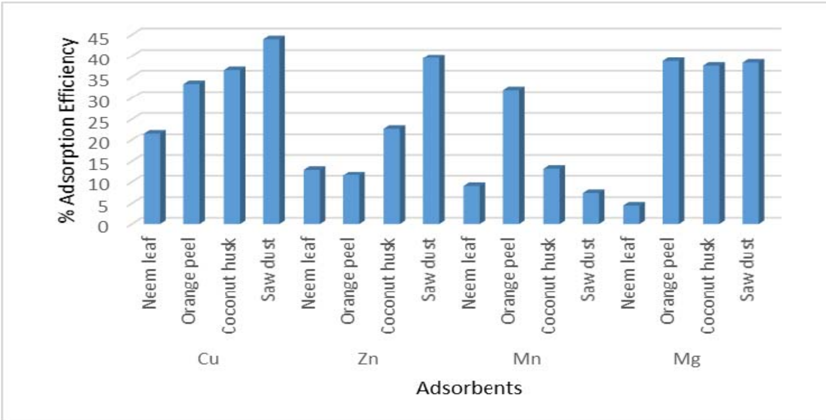

Fig. 2. Adsorption efficiencies of heavy metals for various adsorbents from winery wastewater (www) during non-vintage season

For Cu saw dust appears as most efficient while neem leaf as least efficient adsorbent. For Zn saw dust appears as most efficient and orange peel is least efficient adsorbent. For Mn orange peel appears as most efficient and saw dust as least efficient. For Mg orange peel is most efficient and neem leaf is least efficient.

Figure 3 indicates the adsorption comparison of heavy metals with various adsorbents for pond wastewater (pww) in vintage season. The adsorption of Cu is higher with saw dust and lower with orange peel. For Zn saw dust is the most efficient and neem leaf is the least efficient adsorbent. For Mn coconut husk is the most efficient and neem leaf is least efficient. For Mg coconut husk is again the most efficient and neem leaf a least efficient adsorbent.

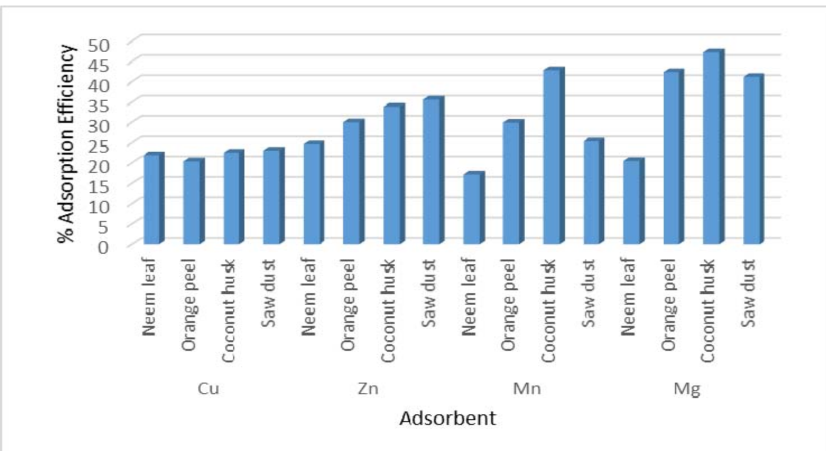

Fig. 3. Adsorption efficiencies of heavy metals for various adsorbents from pond wastewater (pww) during vintage season

Figure 4 indicates the adsorption efficiency comparison for various adsorbents for heavy metals from pond wastewater (pww) during non-vintage season. Here, for Cu again saw dust is most efficient and orange peel is least efficient. For Zn neem leaf is most efficient and orange peel is least efficient. For Mn coconut husk is most efficient and neem leaf is least efficient. For Mg orange peel is most efficient and neem leaf is least efficient.

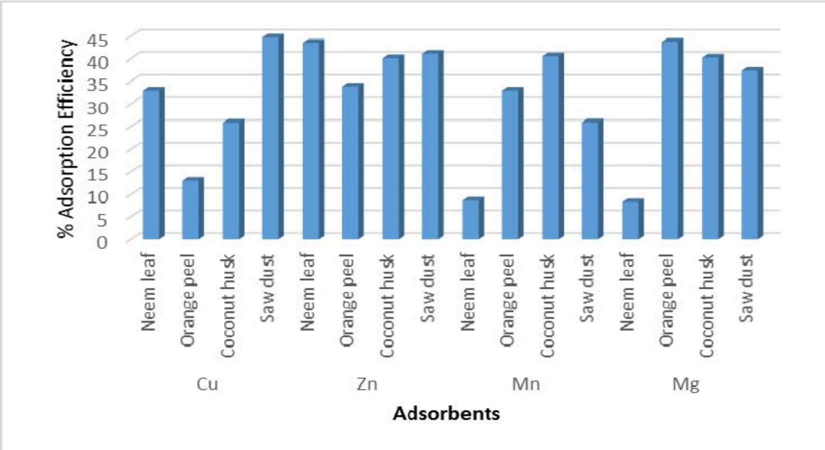

Fig. 4. Adsorption efficiencies of heavy metals for various adsorbents from pond wastewater (pww) during non-vintage season

Thus, the particular adsorbent shows different affinities for different heavy metals. This may be due to the differences in various factors like ionic size and ionic charge for the heavy metals. The study does not take in account the possibility of leaching of heavy metals bio-accumulated on the adsorbent itself due to limitation of instrumentation.

Conclusion

We assessed the efficiencies of some natural adsorbents for the partial removal of some heavy metals from winery wastewater. The adsorbents had good adsorption efficiencies for the metals under study (viz. Cu, Zn, Mn and Mg). No single adsorbent is equally efficient for the adsorption of all the metals under study. Moreover, the efficiency of an adsorbent for the adsorption of a particular heavy metal is also affected by the nature of the sample. For the adsorption of Cu, saw dust is the most efficient adsorbent, followed by coconut husk, among the four adsorbents used for our study, namely neem leaf, orange peel, coconut husk and saw dust. For the adsorption of Zn, saw dust is the most efficient adsorbent, followed by neem leaf. For Mn the most efficient adsorbent is coconut husk, followed by orange peel. For Mg the most efficient adsorbent is orange peel, followed by coconut husk. The method is simple, low cost and effective, hence it may be used for the reduction of heavy metal ion concentrations in industrial effluents on a large scale.

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Received: June, 12, 2013
Accepted: February, 18, 2014