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Low Cost and Eco-Friendly Removal of Toxic Heavy Metals from Industrial Wastewater

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ALTHOUGH water is the most available resource on the earth, its contamination and shortage in many countries make it necessary to find out low-cost and eco-friendly materials to remove heavy metals (HMs) from contaminated wastewater. Thus, this study examined the use of sorbents such as eggshell (ES), banana peels (BP), watermelon rind (WR), and their nano form (ESN, BPN, and WRN) to remove HMs (Cu, Cr, Fe, Pb, and Zn) from industrial contaminated wastewater. All forms of these sorbents were characterized by (Transmission Electron Microscope) TEM and used in the experiment at two addition rates of each sorbent (i.e. 0.5 g and 1.0 g of each normal sorbents and 0.05 g and 0.1 g of each nano studied sorbents in 20 ml). The results revealed high efficiency for removing HMs, especially when using ES, ESN, and BPN. These sorbents achieved nearly 100% removal percentage in all detected HMs in the industrial wastewater especially Cu and Pb. These results demonstrate a high potential use of the studied sorbents for HMs removal from contaminated wastewater especially nano forms due to their unique properties and higher surface area.

Keywords: Eggshell; Banana peels; Watermelon rind; Nano sorbent; Heavy metal removal; Contaminated wastewater.

Introduction

Water plays a vital role in the natural environment, hence the persistence of life on Earth. (Rai 2012; Tantawy et al., 2015; Thirumdas et al. 2018; Saha and Rahman 2018). Thus water security is amongst the top five global crises regarding development impacts (Amare et al. 2017). In addition, water bodies' contamination by HMs through discharging industrial wastewater is a worldwide environmental issue that needs to be properly addressed. Rapid industrialization has seriously contributed to the release of potentially toxic HMs to water streams (Ahmaruzzaman 2011; Reddy et al. 2011; Islam et al. 2016; Saha and Rahman 2018; Aitta et al., 2019; Shahedi et al. 2020; Eldamaty et al., 2021). Heavy metals such as Cu, Fe, Ni, Pb, and Zn are among the most common inorganic contaminants found in industrial wastewater (Reddy et al. 2011). They could represent a risk to humans, flora, and fauna of the receipt water bodies (Jawed et al. 2020).

Water resources limitations, shortage, and crisis as well as the importance of reusing water, makes it necessary to find eco-friendly methods for contaminants removal to reuse it (Samani et al. 2010). Hence, finding low-cost and eco-friendly treatment materials of water and wastewater without generating hazardous by-products has been broadly investigated (Hokkanen et al. 2016). Adsorption is a trendy and economical treatment method that has been utilized to remove different types of HMs owing to its easiness, efficiency, and eco-friendliness (Jawed and Pandey 2019). Low cost and agricultural wastes are gaining attention in the water treatment process because of their ability to eliminate different types of HMs. Most of the non-traditional adsorbents that are made from low-cost materials have a high surface area to their volume ratio and large amount of active binding locations such as–OH, –COOH, $–NH_2$, and –SH groups that can efficiently bind and remove HMs. Thus, these adsorbents are the most economical that available with plentiful

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sources (Rudi et al. 2020). Among the agricultural wastes, banana peels are abandoned agro-wastes discarded worldwide as useless material, thus causes waste management problems. However, it is readily available, low cost, and cheap, and environment-friendly bio-adsorbent. In addition, it has shown high performances in the adsorption process (Hossain et al. 2012; Ahmad and Danish 2018; El-Ramady et al., 2020; Kim et al. 2020). In addition, watermelon rind is an agro-waste discarded in significant quantities nearly 30% of the overall fruit mass and it has many features making a favorable platform for the production of activated C materials making it an effective binding material for HMs (Bhattacharjee et al. 2020). Furthermore, eggshell is resulted from the industry of food processing as an abundant biowaste without being treated in advance as useless and represents about 11 % of egg weight with its associated ES membrane (Jendia et al. 2020; Peigneux et al. 2020).

Recently, nano-adsorbents used widely as an advanced technology for wastewater treatment. Their smaller size increases their surface area which improves their chemical activity and adsorption capacity to adsorb HMs on their surface. In addition to its high surface area, the external functionalization of nano-adsorbents provides them their physical, chemical, and material characteristics which influence the adsorption in the aqueous environments (Anjum et al. 2019). Some researchers effectively used the low-cost and agricultural waste for HMs removal, as well as other pollutants, from aqueous solution such as Arunlertaree et al. (2007) (ES to remove Pb from battery manufacturing wastewater); Jai et al. (2007) (calcined ES to remove Cr from electroplating wastewater); Anwar et al. (2010) (BP to remove Cd and Pb from contaminated aqueous solution); Liu et al. (2012) (BP and WR to remove Cu from contaminated aqueous solution); Mahmoud (2014) (BP to remove Mn from raw groundwater); Othman et al. (2014) (WR to remove Zn from wastewater mosaic industry); Reddy et al. (2014) (WR to remove Cr from tannery effluents); Gomaa (2017) (BP and WR to remove Fe from contaminated aqueous solution); Husein et al. (2017) (WR to remove Cd from Red Sea water, Al-Arbaien Lake water and tap water); Shakoor et al. (2018) (WR to remove As (V) from groundwater from drinking water of rural areas); Chen et al. (2020) (WR to remove Cd, Cu, and Ni from contaminated aqueous solution); Jendia et al. (2020) (ES to remove nitrate from groundwater). However, most of the previous works used the above-mentioned on contaminated aqueous solutions almost on mono metal, not on industrial solutions. In addition, few works have explored the importance of nano above-mentioned waste to remove HMs from aqueous solutions such as Oyewo et al. (2016) (BP to remove U and Th from mining water) and Setiawan et al. (2018) (nanoporous of avian ES to remove Cd, Cr, and Pb from water filters containers that commonly used in pure and contaminated groundwater). Therefore, yet there is a lack of knowledge concerning the utilizing of these low-cost materials in HMs removal from contaminated wastewater especially industrial wastewater. Therefore, this study aims to investigate the effectiveness of low-cost and eco-friendly materials (ES, BP, and WR) to remove toxic HMs from industrial wastewater, and also to examine the effectiveness of nano forms of these waste in the same purposes.

Materials and methods

Wastewater sampling and analysis

Samples were collected from the main drainage pipe of a cartoon factory in the industrial area at Quesna, Al -Menofia governorate, Nile Delta, Egypt. Location map demonstrated in (Figure1) as taken from Google Earth. Polyethylene bottles were washed many times with distilled water. To avoid microbial degradation, the samples were immediately acidified after filtering (pore size=0.45 µm) with adding 2 ml ultra-pure HNO_3 /L and then carefully kept in a refrigerator at 4 °C until analysis. Physiochemical properties of water samples including pH, electrical conductivity (EC), total dissolved solid (TDS) were measured by (Mi170, Milwaukee, Italy) according to standard methods for the water and wastewater examination by American Public Health Association (APHA 2005).

To measure HMs, 20 mL of wastewater sample was digested with 1.5 mL HNO_3 hydrochloric acid, and 30% hydrogen peroxide. The digested samples were then moved into a Teflon beaker and the total volume was completed to 50 ml with distilled water. The digested solution was then filtered by a Whatman no. 42 filter paper and was kept in polypropylene tubes. Blank samples without wastewater were digested also. The total HMs concentration were analyzed by Atomic Absorption Spectrometry (GBC Avanta E, Victoria, Australia) according to standard methods also according to (APHA 2005). To ensure the measurement precision, standard reference material (provided by Phenova; WS0718) with known concentrations of measured metals were used as control samples and analyzed after every three water samples to confirm the analysis accuracy. All samples were measured three times to evaluate the measurement repeatability and to eliminate any batch-specific error. All reagents were of analytical grade.

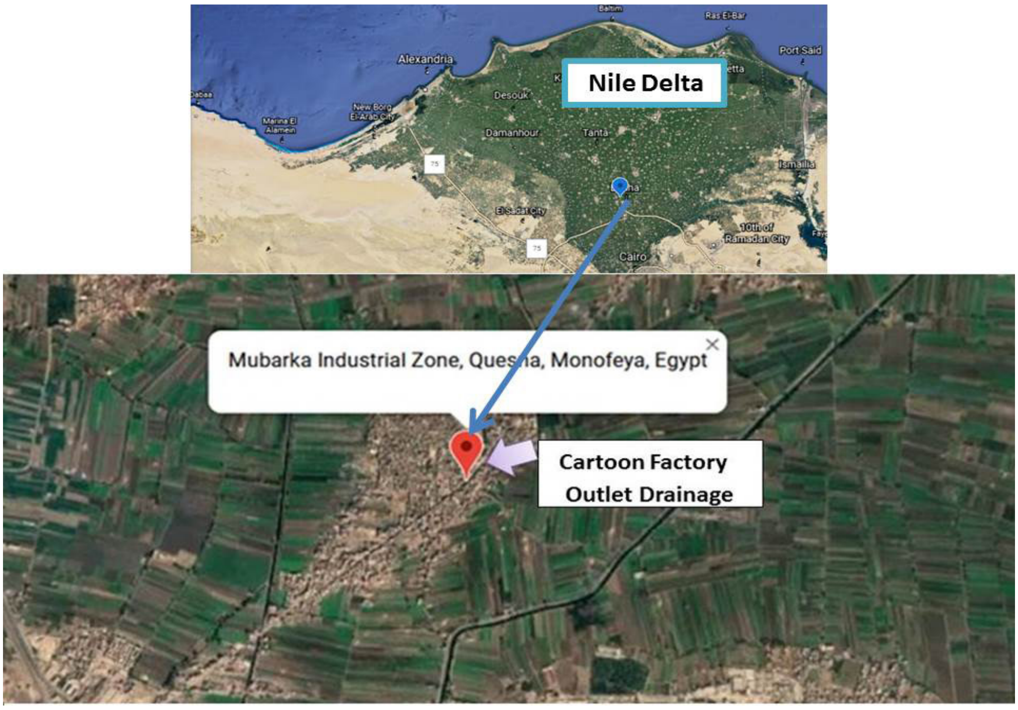


Fig. 1. Wastewater location on the Nile Delta, Egypt Map as taken from Google Earth software

Sorbents: Sampling, preparation and characterization

Normal sorbents

(BP, ES and WR) were collected from the nearby locality (Dakahlia Governortae), washed by tap water, and rinsed many times in distilled water. The samples were cut into appropriate size and then sun-dried for 10 days. The sundried samples were oven dried under 80 °C for about 24 h. All samples were ground to powder form and stored in an airtight container until analysis and usage in the experiment

Nano sorbents

Samples were prepared by standard ceramic method Mahadule et al. (2013) as follows: The above-mentioned sun-dried samples were oven dried at 200 °C for about 6 hr. All samples were ground to powder by ceramic mortar for about 9 h and kept in an airtight container until characterization, analysis, and using in the experiment to remove heavy metals from aqueous solution.

Sorbents characterization

The sorbents morphology was studied using Transmission Electron Microscope (TEM) (JEOL, JEM2100 Japan). Sorbents pH was measured in deionized water (1: 2.5 for inorganic sorbents, and 1:10 for organic sorbents) according to Thomas (1996). Organic matter content was determined by the Walkley-Black method Walkley (1947), while total calcium carbonate equivalent was determined using Collins calcimeter Collins (1906).

Removal of heavy metals from contaminated wastewater

A batch equilibrium experiment was conducted to examine the effectiveness of studied sorbents in the removal of heavy metals in the wastewater sample as follows: 0.5 g and 1.0 g of each normal studied sorbents and 0.05 g and 0.1 g of each nano studied sorbents was equilibrated with 20 ml of studied contaminated wastewater. Samples were placed and mixed for 24 h on a reciprocating shaker at room temperature. After equilibrium, the samples were centrifuged and the supernatant was filtered through a Whatman No.42 filter paper. Heavy metal concentrations in the supernatant were measured by Atomic Absorption Spectrometry (GBC Avanta E, Victoria, Australia) according to standard methods for the examination of water and wastewater (APHA 2005). The removal percentage values were calculated as in Eq.:

$$\text{Removal percentage } \% = ((C_0 - C_{eq})/C_0) * 100$$

where: C_0: initial concentration (mg L^{-1}); C_{eq}: equilibrium concentration (mg L^{-1}).

Statistical analyses

The obtained data were statistically analyzed using SPSS 20 software (IMB SPSS Statistics Software, Armonk, New York). Statistical analysis was performed with analysis of variance. Duncan's multiple range tests were used to compare the means of the treatments, variability in the data was expressed as the standard deviation, and $P < 0.05$ was considered to be statistically significant.

Results and Discusion

Characteristics of wastewater

The characteristics of wastewater sample were presented in Table 1. The pH of wastewater was approximately neutral (6.94), which is slightly acidic. Lower pH makes the wastewater may cause potential detrimental impacts and may react with other materials such as HMs and causes toxicity (Islam et al. 2016). The EC was 4.57 dSm^{-1} which means potential increasing water salinity which may disrupt the aquatic life (Nielsen et al. 2003). In addition, if this wastewater is discharged in the agricultural soils or used in irrigation, it will cause soil salinity. The value of TDS was 2.29 g L^{-1}. The HMs concentration in the sample was in the following order Fe (1080.00 mg L^{-1}), Cr (754.00 mg L^{-1}) and Pb (7.82), while Cd and Ni were not detected. All detected HMs in the samples exceeded the average of waster in a river (Kabata-penedias, 2011), Egyptian Environmental Requirements of industrial wastewater (EEAA 2003), the permissible limits of the irrigation waters (FAO 1985), and maximum limits of drinking water (WHO 2008).

Characterization of studied sorbents

Transimition Electron Microscope image (TEM) for studied sorbents

The TEM image for normal sorbents shows the particle size of studied sorbents (Figure 2: a, b, and c). The average particle size of ES, BP, and WR ranged from 1.73 to 3.85, 1.34 to 5.67and 1.05 to 4.26 µm respectively. On the other hand, the TEM images of nano-sorbents (Figure 2: d, e, and f) revealed that an average size of ESN, BPN, and WRN ranged from 12.60 to 24.24; 7.89 to 11.82; 9.75 to 30.23 nm respectively.

Physiochemical characterization of studied sorbents

The physicochemical characterization of studied sorbents (ES, ESN, BP, BPN, WR, and WRN) are presented in (Table 2). The pH of ES, ESN, BPN, and WRN was alkaline; 8.71, 8.25, 7.46, and 7.30 respectively, while BP and WR were acidic with pH of 5.81 and 6.00 respectively. The ES and ESN have high CaCO3 concentrations; 98%. These results of ES calcium carbonate were in agreement with (Shaheen et al. 2013). On the other hand BP, BPN, WR and WRN have low CaCO3 concentration of 5.81, 6.47, 7.47, and 7.43 respectively. The BP and BPN recorded the highest percentage of organic C concentrations (3.82 and 3.78 respectively), while ES and ESN recorded the lowest values of organic C (1.0 and 0.7 respectively).Organic matter (then organic C) may affect negatively or positively the HMs availability due to the formation of HMs complexes (Sweed, 2019). Thus it is expected that BP follow this trend with studied HMs. Also, Abbas and Bassouny (2018) stated that the fraction of the organic matter that dissolves in water can form soluble organo-metal complexes.

Removal efficiency of heavy metals from contaminated wastewater

The removal percentage of Cr, Cu, Fe, Mn, Pb, and Zn metals by the examined sorbents from contaminated wastewater is presented in Fig. 3 (a, b, and c). The results revealed that the removal efficiency of investigated HMs differed widely among the HMs. Also, all the studied sorbents revealed high removal efficiency of all metals. The ES, at both addition rates, revealed the highest removal percentage of all studied metals. On the other hand, ESN showed a different trend compared to ES, where the removal percentage was lower in all studied metals except Cu and Pb (their removal percentage was higher than 99.9%)

TABLE 1. Characteristics and metal concentrations in the studied wastewater

Wastewater and allowable limits of metals	PH	EC dSm^{-1}	TDS g L^{-1}	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
				mg L^{-1}							
Studied wastewater	6.94	4.57	2.29	nd	754.00	20.70	1080.00	10.97	nd	7.82	20.70
Maximum limits of drinking water (WHO 2008)	6.5-8.5	-	-	0.005	0.05	1	0.3	0.05	-	0.05	5.0
Maximum conc. in irrigation water (FAO 1985)	-	-	-	0.01	0.10	0.20	5.0	0.20	0.20	5.0	2.0
Industrial wastewater (EEAA 2003)	6-9	-	-	-	1	1	1	-	-	-	-

EC: Electrical conductivity; TDS: Total dissolved solids; nd: non-detected.

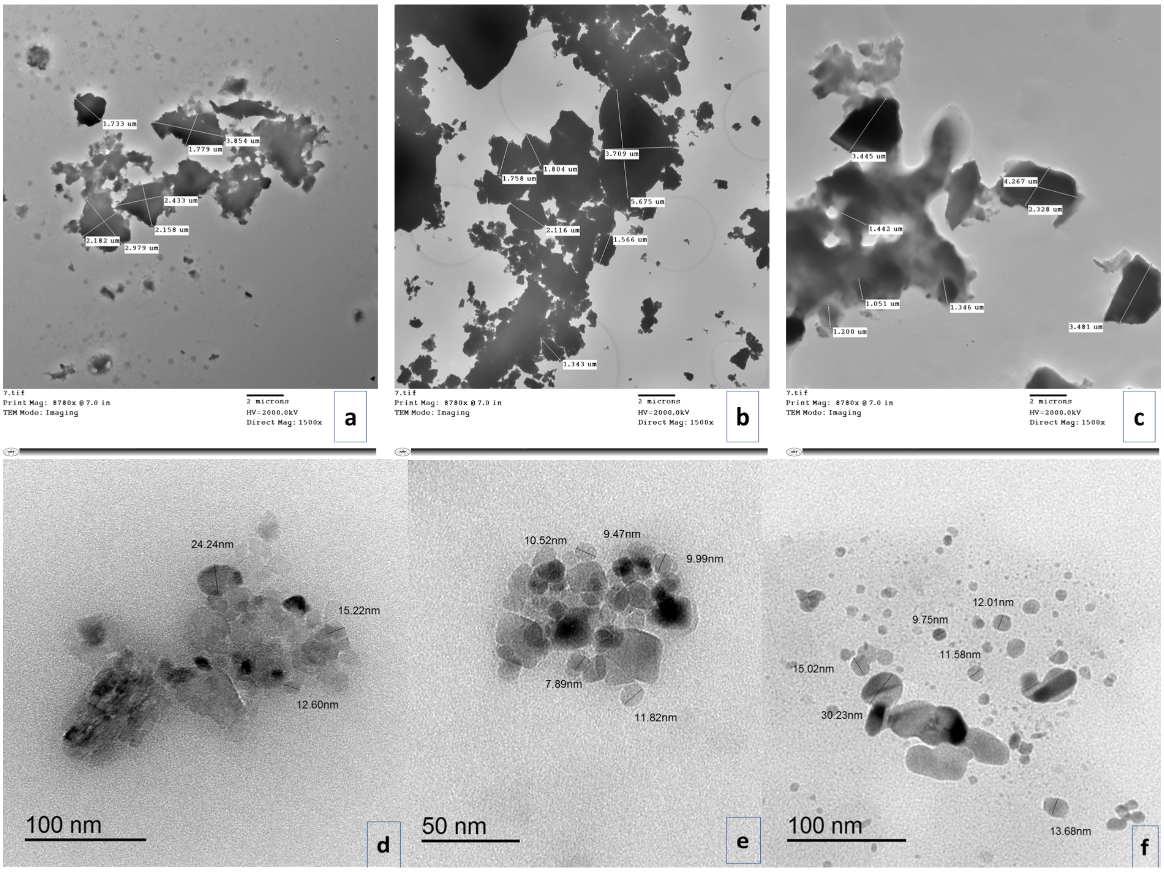


Fig. 2. TEM images of normal (a) ES, (b) BP, and (c) WR and nano sorbents ESN(d), BPN (e), and WRN (f)

TABLE 2. Characteristics of the studied sorbents

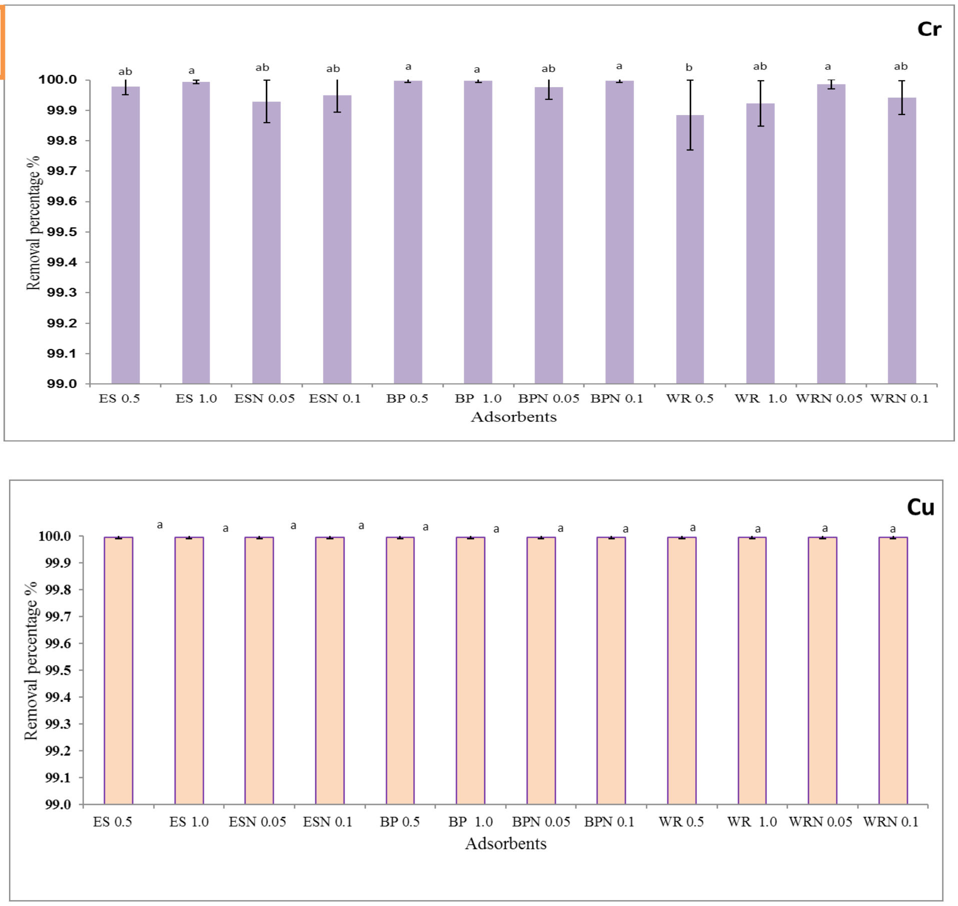
Parameters	ES	ESN	BP	BPN	WR	WRN
pH	8.71	8.25	5.81	7.46	6.00	7.30
Organic C (%)	1.0	0.7	3.82	3.78	1.73	1.31
$CaCO_3$ (%)	98	98	5.81	6.47	7.47	7.43

Abbreviations: ES: Eggshell Normal; ESN: Eggshell Nano; BP: Banana Peel Normal; BPN: Banana Peel Nano; WR: Watermelon Rind Normal; WRN: Watermelon Rind Nano

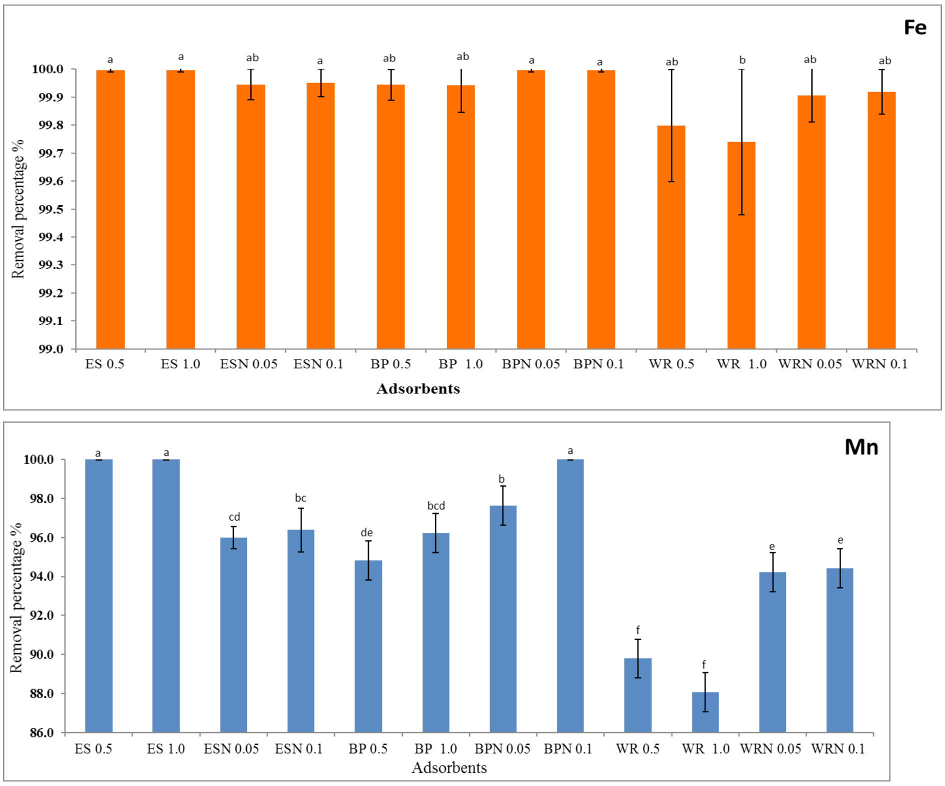
with insignificance difference. Tabatabaee et al. (2016) found that ES has a greater ability to absorb Cd, Cr, and Pb from water compared to other their studied adsorbents (almond skin, sawdust, walnut shell, and rice bran) and ascribed this to its greater absorption capacity. In the presence of various metal ions, there is a competition among them for the coordination sites present on the surface of adsorbent. The high surface area of BP adds to the property and makes it an excellent and economic adsorbent, for the water purification process (Darge and Mane 2013).

Our results revealed that BPN, especially at addition rate 0.1 g was the highest in removal of all studied metals, as well this demonstrated at addition rates 0.05 g for all studied metals except Mn (97.63)%. However, BP with its two additional raes removed Cr, Cu, and Pb. Anjum et al. (2019) reported that nano-adsorbents have many features making it better to remove heavy metals such as high surface area, high dispersion ability, and microporous structure. This may interpret that efficiency of BPN to remove 100 % of metals at a higher addition rate. The results in Table (2) showed that the BP and BPN were higher in their content of organic C than other sorbents. Ahmad and Danish (2018) and Kim et al. (2020) stated that the banana peels waste contain C-rich organic compounds such as cellulose, hemicellulose, pectin substances, and some other low molecular weight compounds which have a strong binding capacity to the metal cations in the aqueous phases due to the existence of some active functional groups.

a


Cr
Cu
Removal percentage %
100.0
99.9
99.8
99.7
99.6
99.5
99.4
99.3
99.2
99.1
99.0
ES 0.5
ES 1.0
ESN 0.05
ESN 0.1
BP 0.5
BP 1.0
BPN 0.05
BPN 0.1
WR 0.5
WR 1.0
WRN 0.05
WRN 0.1
Adsorbents

b


Fe
Mn
Removal percentage %
100.0
99.9
99.8
99.7
99.6
99.5
99.4
99.3
99.2
99.1
99.0
98.0
96.0
94.0
92.0
90.0
88.0
86.0
ES 0.5
ES 1.0
ESN 0.05
ESN 0.1
BP 0.5
BP 1.0
BPN 0.05
BPN 0.1
WR 0.5
WR 1.0
WRN 0.05
WRN 0.1
Adsorbents

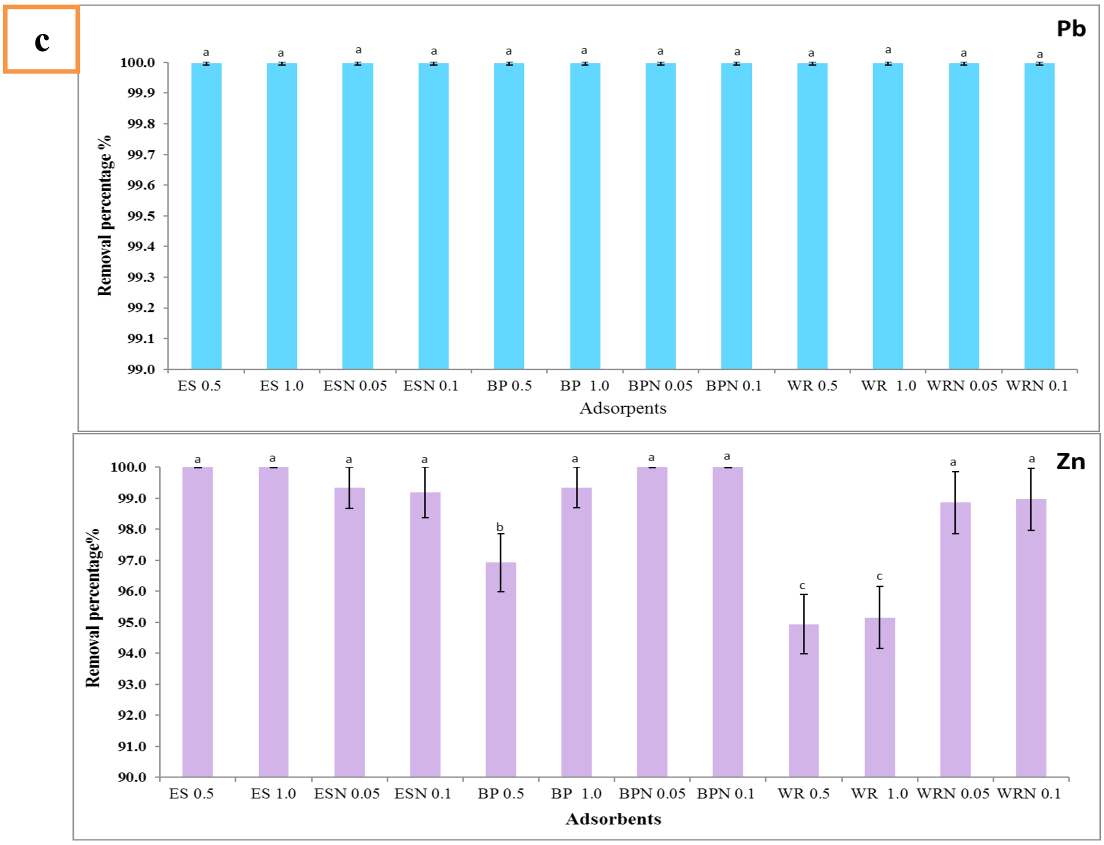


Fig. 3. Removal percentage of Cr, Cu (a), Fe, Mn (b), Pb, and Zn (c) from wastewater samples by the studied sorbents

The high efficacy of normal ES and BPN may be due to their alkalinity (PH 8.71, and 7.46) respectively. Thus, they can be used for increasing pH of the solutions, reducing metals solubility due to enhanced sorption and/or precipitation. Inorganic C (such as ES) formed manily of elemental C and carbonate minerals (Elbasiouny and Elbehiry, 2019). As well, the relative ES high ability for HMs sorption may be attributed of its high $CaCO_3$ content (98%) as also stated by Ahmad et al. (2012). Our results are in accordance with (Aziz et al. 2008) who reported that presence of calcite buffers pH and increase the removal efficiency of HMs according to two effects: the rough surface of the limestone gives solid contact resulting in strong sorption of HMs ions and the existence of dissolved $CaCO_3$ had elevated the solution pH higher than the solubility point causing metals precipitation as metals oxide and maybe metals carbonate (Ali, 2017). For BP, the surface activity is mainly because of the presence of carboxyl, hydroxyl and amide groups at its surface which make it can chelate several metals and help in their removal (Ali, 2017).

The removal percentage showed a different trend with WR and WRN where it was the highest at both addition rates in Cu and Pb (100%) and the lowest in Mn. These results agreed partially with Liu et al. (2012) which noticed that in multi-metals solution, the selectivity order in the investigated range was observed to be Pb(II) > Cu(II) > Zn(II), which indicates the better affinity of WR especially for Pb, as well they observed that ion exchange and micro-precipitation which occurred on the surface area were estimated to be the main biosorption mechanisms. The highest removal of WR and WRN may be due to functional group of -COOH in the watermelon (denoted as -COOH) will coordinate with Cu^{2+} ions to form –COO-Cu^{2+} -OOC-, thereby enabling the Cu^{2+} ions in the aqueous solution to be adsorbed effectively (Gupta and Gogate 2016). In addition, Bhattacharjee et al. (2020) added that WR is comprised of carbonaceous substances such as cellulose, pectin, carotenoids as well, it has low molecular weight substances such as amino acid, citrulline and other phytochemical compounds. As well, the experiments have also revealed that the WR has a significant amount of phenolic substances possessing a high radical scavenging capacity (OH radical scavenger), which makes it favorable to remove HMs because of its effective binding to them. Lakshmipathy and Sarada (2016) reported preferential sorption of Pb^{2+} ions during multi-metal biosorption using WR rind and attributed this to high electro-negativity and smaller ionic radius of Pb ions. As well, Anastopoulos et al. (2019) noticed that the adsorption using WR is based on the interaction between the hydroxyl, amino and carboxylic groups present on the adsorbents surface and the metal such as Cu^{2+}, Pb^{2+} and Cr^{3+} anions which indicates the formation of strong inner-sphere complexes as well indicates that the adsorption mechanism is described as an ion exchange process.

Thus, all studied sorbent revealed different behavior with all studied metals except Cu and Pb (their removal percentage are 100% with all studied sorbent). This could be attributed to the Cu and Pb chemical characteristics; relatively high electronegativity, lower pK_H (negative log of hydrolysis constant), small hydrated radius, and their electronic structure, which makes these metals are adsorbed stronger (Appel et al. 2008; Shaheen et al. 2013). Stevenson and Arkadani (1972) also stated that Cu has the highest affinity to organic matter because of forming inner–sphere complexes, and signified this as chemisorption or specific sorption. Zhou and Wong (2001) reported that Cu almost correlated with organic adsorbents due to the high steadiness constants of their organic complexes. The Cu sorption by organic substances occurs through coordination with O functional groups like COOH, phenolic OH, C=O (Yuan et al. 2002).The high adsorption performance for Pb may be due to its larger atomic weight, ionic radius with smaller hydrated radius and first hydrolysis constant all of this makes Pb a better adsorbate than other metals through complexation reactions on sorbent surface as reported by (Abdin et al. 2020). Trakal et al. (2012) also reported that among various heavy metals Pb has a great affinity towards sorption sites and that the presence of any other metals does not affect Pb sorption due to its lower chemical stability.

Conclusions

Low cost and ecofriendly adsorbents were used to investigate the removal efficiency of Cr, Cu, Fe, Mn, Pb, and Zn from industrial wastewater. Eggshell, banan peels, watermelon rind, and there synthesized nano forms were effectively achieved high removal efficiency in all investigated heavy metals. Eggshell at two addition rates revealed the highest removal percentage of all studied metals except for Cr, however, its nano form showed a different behavior where the removal percentage was lower in all studied metals except Cu and Pb which achieved 100% removal percentage. The nano form of banana peels, at two addition rates exhibited the higher removal of all studied metals except for Cr and Mn at addition rate of 0.05 g than its normal form. On the other hand, the removal percentage was similar in watermelon rind and its nano form where it the highest at two addition rates in Cu and Pb (100%) and the lowest in Mn. As a result, eggshell and banana peel nano form possesses prospective application for the removal of heavy metals in wastewater treatment due to inexpensive, easily available, cost-effective and highly efficient in adsorbing different kind of heavy metal ions.

Author contribution

This study was designed and carried out by the authors, and all authors participated in the writing the paper, interpreting the information provided, and reading and agreeing to the final version of the article.

Conflict of interest

The authors declare there is no conflict between them

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