The Adsorption of Cadmium, Nickel, Zinc, Copper and Lead from Wastewater using Tea Fiber Waste

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Abstract: The feasibility of tea fiber waste to remove cadmium, nickel, zinc, copper and lead from wastewater was studied in the present research. The tea fiber was treated with ferric oxide and nitric acid solution and the properties like surface area, pore volume and particle size were improved. The surface characteristics of the adsorbent was determined using SEM and FTIR analysis. Isotherm models such as Langmuir, Freundlich, Flory Huggins, Temkin and Dubinin Radushkevich models were used to investigate the isotherm data in the single solution mode. The data were matching better with the Freundlich model compared to other models. The adsorbent treated with ferric oxide was showing better in comparison with the adsorbent treated with nitric acid mainly because of surface properties. The interaction mechanism in the quinary solution showed synergism for cadmium, zinc and lead and antagonism for nickel and copper.

Key words: Tea fiber, surface morphology, toxic metal, isotherm, multicomponent, interaction

INTRODUCTION

Water is considered as one of the resource required for all the living species in the environment (Rathinam et al., 2019). The increase in global population is leading to rapid industrialization and urbanization and thus, releases wastewater into the aquatic system and agricultural land (Mohan, 2014; Prelot et al., 2018). At the same time, disposing of the industrial waste in an irregular way, especially in developing countries results in environmental issues. This wastewater contains all the pollutants like toxic metals, dyes and organic compounds (Verma and Sarkar, 2018). Hence, the industrial wastewater is a multicomponent mixture having different pollutants and the treatment of these components is a major challenge (Costa et al., 2018). The components will interact and compete among each other and it is important to understand the overall behavior of the system (Loganathan et al., 2018). Also by studying the competitive interaction (synergistic or antagonistic) among the pollutants, the mobility of these components can be understood and treatment can be implemented effectively (Du et al., 2018). Toxic metals which are the major pollutants in wastewater are having adverse effects on the human health and aquatic system (Rathinam et al., 2019; Wang and Chen, 2018). Also because of the non-biodegradable and high mobile nature of these metals in the environment, it enters the food chain and affects the ecosystem (Arim et al., 2018; Niu et al., 2018). The environmental protection agencies, defines some of the toxic metals copper, nickel, zinc, cadmium and lead as priority pollutants because of its harmful effects (Anna et al., 2015). Thus, the current research investigates treatment of these metals from multicomponent solution.

Copper is one of the toxic metal which is found in the wastewater released from industries like electroplating, hydrometallurgy, mining, metal coating, electroplating and painting industries (Nashtifan et al., 2017; Zhou et al., 2017). It is considered to be one of the transition metal ion required for functioning of biological processes in the human body. It is necessary for functioning of enzymes and development of bones for the human beings. But however, when the metal quantity exceeds the maximum limit, it results in carcinogenic problems, effects central nervous system, respiratory system and causes gastrointestinal diseases and anaemia (Nashtifan et al., 2017; Zhou et al., 2017). The presence of metal in the water bodies also affects the aquatic life and the environment. As per the World Health Organization the allowable concentration of copper in drinking water should be lower than 2.0 mg/L and the Indian standards
have recommended the permissible concentration of copper as 0.05 mg/L in the water sources (Chatterjee et al., 2017; Zhou et al., 2017).

Zinc is one of the important metal used in industries such as ceramics, rubber, fabrics, metal coating for corrosion prevention, mining manufacturing and battery. Its salts are used for preparing catalysts, wood preservatives and photographic paper. Zinc is present in the wastewater released from acid mines and galvanizing industries. Baig et al. (2009), Chatterjee et al. (2017) and Ray et al. (2018) World Health Organization defines the allowable concentration of zinc in the drinking water <5.0 ppm (Baig et al., 2009; Chatterjee et al., 2017). The excess quantity of zinc causes various harmful effects to aquatic bodies and the human beings. It causes depression, nausea, diarrhea, lethargy, restlessness, skin irritations and vomiting (Ray et al., 2018; Sükpreabprom et al., 2015). It is non-biodegradable and enters the plant cells, animals and humans through food chain causes adverse effects (Ray et al., 2018).

Cadmium is associated from industries like mining, battery, stabilizers, fertilizers, enameling and plating industries (Bozorgi et al., 2018). As per the environmental regulation agencies, the permissible level of cadmium in drinking water is 0.001 mg/L (Belyakova et al., 2014). It is non-biodegradable compound that enters the human metabolism system through food chain (Sükpreabprom et al., 2015). Its excess to human beings causes anemia, dis-functioning of liver, kidneys, lungs, cancer, skeleton damage and results in other problems memory deterioration (Belyakova et al., 2014).

Lead is an important pollutant from the paints, explosives, photographic materials, glass operating, plating, petrochemical, oil, pigments and rubber industries (Kakavandi et al., 2016; Kavand et al., 2014). Higher exposure of lead to human body causes mental retardation, encephalopathy, kidney damage, gastrointestinal damage, liver damage, hypertension and reduces haemoglobin production (Hossain et al., 2014; Mohan 2014). It should be taken precaution that the concentration of 0.1 mg/L of lead into water bodies allowed as per the environmental regulations (Kavand et al., 2014).

Nickel is one of the toxic metal released from industries such as battery, electrolyzing, plating, paint, mining, metallurgy, battery and fertilizer industries (Arim et al., 2018; Neshifan et al., 2017). The wastewater from the metal plating industries contains nickel in the range 6-12 mg/L (Kavand et al., 2014). At higher concentration, nickel is having harmful effects such as gastrointestinal irritation and lung, kidney problems, skin dermatitis, headaches, dizziness, chest pain and other health problems (Kavand et al., 2014; Zeledon-Toruno et al., 2005). The maximum allowable concentration of nickel in drinking water as per environmental protection agencies is 0.1 mg/L (Baig et al., 2009).

A large number of treatment methods such as chemical precipitation, electrolysis, membrane separation, ion exchange, flotation, coagulation and adsorption are used for treating toxic metals from wastewater (Bozorgi et al., 2018; He et al., 2018a, b). Among the above methods, adsorption using adsorbent is considered to be effective method for treating toxic metals from aqueous solution (Sreedharan et al., 2017). It has greater efficiency for removing variety of pollutants, easy to operate, economically feasible (Zhou et al., 2017). It has the advantages of simplicity in process design and can selectively remove specific pollutants from a multicomponent mixture (Xu et al., 2018).

The adsorbent produced from non-renewable sources has higher adsorption capacity. But considering the cost of the adsorbent there is a need to produce the adsorbent from low cost agricultural waste materials (Du-Gama et al., 2018). Therefore, in the present study an effort has been made to produce the adsorbent from tea fibre waste. Thus, the adsorbent is used to remove the toxic metals copper, nickel, zinc, cadmium and lead from wastewater.

MATERIALS AND METHODS

Chemicals used: The chemicals nickel chloride hexahydrate (Merck India Limited), cadmium nitrate tetrahydrate (Finar Ltd), lead nitrate (Finar Ltd), cupric nitrate trihydrate (Finar Ltd) and zinc sulphate heptahydrate (Finar Ltd) were used for preparing the solutions. The other chemicals ferric oxide red (Finar Ltd), nitric acid (Fischer Scientific Ltd), sulphuric acid (Merck India Limited) and sodium hydroxide pellets (Fischer Scientific Limited) were used in the experiments.

Adsorbent preparation: The tea waste fibres were obtained from tea plantation from Sivasagar, Assam and used for adsorbent preparation. The material was thoroughly washed with distilled water to remove the dirt particles and later the slurry was stirred with mechanical stirrer and then allowed to settle. After the settling process, the top layer containing water with the dirt particles are separated. The bottom layer having the material was dried in oven at 110°C for 2 days to remove the moisture content. The slurry was stirred every 3 h and the drying process was checked. Later 50 g of dried powder was mixed separately with 200 mL of 0.2 M nitric acid and 200 mL of 0.1 M ferric oxide solution for 20 min. Then the slurry formed was heated inside muffle furnace at 550°C for 1 h and 550°C for 1.5 h for nitric acid solution and ferric oxide solution, respectively. Later, the dried
samples were washed with water to remove all the excess chemicals. The washing process was carried out continuously, so that, the pH value comes to 7-8 (Moreno-Castilla, 2004). Finally, the water content is removed, the slurry is dried in the oven at 80°C and used for the experiments.

Characterization of the adsorbent: The proximate analysis of the raw material was carried out to calculate the moisture content, volatile matter, ash content and fixed carbon using standard procedure (APHA et al., 1989). The pore volume and surface area were measured with BET apparatus (Smart Instruments, India). The particle size was found using particle size analyzer (CILAS 1064, France). The functional groups existing on the adsorbent surface were analyzed using Fourier Transform Infrared spectroscopy (FTIR) instrument, Shimadzu, Japan. The surface structure of the adsorbent was obtained by Scanning Electron Microscopy (SEM), Zeiss Company, Germany. The confirmation of the presence of metal ions on the surface were carried out using Energy Dispersive X-ray (EDX).

Batch experiments: The batch studies were performed in 250 mL flask having 200 mL of different pollutants like copper, zinc, nickel, cadmium and lead. The metal solutions were prepared in the concentration range varying from 5-25 mg/L. The isotherm experiments in the single solution mode were conducted by taking the different solutions individually in the concentration range of 5-25 mg/L of all the metals copper, zinc, nickel, cadmium and lead. The adsorption studies were carried out separately by mixing the solutions with 0.5 g of the ferric oxide and nitric acid treated adsorbent at pH 7, 28°C. It is subjected to agitation in a shaker at a stirring speed of 125 rpm for the equilibrium time of 12 h. The multicomponent studies were conducted by combining all the pollutants in quinny solution mode. The quinary solution consists of 40 mL of 25 mg/L concentration solution of all the five components in the 250 mL flask. The experimental conditions were maintained similar as that of the single solution mode experiments. The flasks were agitated inside the shaker till the equilibrium time. Then the residual concentration of the solutes in the multicomponent solutions were analyzed with the help of atomic absorption spectrophotometer (Thermo Scientific, Australia). The concentration of lead, cadmium, nickel, copper and zinc were measured at a wavelength of 217, 228.8, 232.1, 324.8 and 213.9 nm, respectively.

RESULTS AND DISCUSSION

Adsorbent characterization

Surface properties of the adsorbent: The proximate analysis of the raw material as given in Table 1 showed fixed carbon content of 48.18% suggesting that the material was suitable for the adsorption process and potential capacity to remove the pollutant (Elizalde-Gonzalez and Hernandez-Montoya, 2009). By treating the adsorbent with ferric oxide and nitric acid solution the surface properties such as the pore volume and pore diameter were improved (Jung et al., 2017). The average particle size was obtained as 106.31 and 109.85 μm for adsorbent treated with ferric oxide and adsorbent treated with nitric acid, respectively which shows that it assists in the accumulation of the pollutant. The surface properties for both the adsorbent treated with ferric oxide and adsorbent treated with nitric acid obtained are shown in Table 2. These values were promising and suggests that the adsorbent have capability in accommodating larger number of solute molecules in the pores of the adsorbent (Salman and Hameed, 2010).

FTIR analysis of the adsorbent: The FTIR spectra of the ferric oxide treated and nitric acid treated adsorbent before and after adsorption are given in Fig. 1-4. In the ferric oxide treated various peaks are formed are discussed below. The peak at 570.93 cm⁻¹ was assigned to vibrations of Fe-O bonding of iron oxide (Shiomi et al., 2014). The C = C bond of alkenes is shown for the peak at 2208.49 and 2212.35 cm⁻¹. The peak at 331.07 and 331.37 cm⁻¹ are because of O-H vibrations of carboxylic group (He et al., 2017). The peak at 1598.9 and 1593.2 cm⁻¹ are ascribed to hydrogen bonding of carboxyl group (Anirudhan et al., 2009). The C-H functional group peak was observed at 3072.9 cm⁻¹ (Gupta and Balomajumder, 2017). The formation of these bonds on the adsorbent surface and the changes in the peaks of these functional groups were responsible for the adsorption of pollutant on the adsorbent surface.

In the adsorbent treated with nitric acid, the peak found at 3547.09 cm⁻¹ is because of N-H bonding of amines proving the formation of amino group on the treated carbon. The peak obtained at 1128.36 and 1134.14 cm⁻¹ are due to C-O stretching mode (Kumar et al., 2018). The peak at 3350.35 cm⁻¹ is because of hydroxyl group obtained from the cellulose group (Costa et al., 2018).

### Table 1: Proximate analysis of the raw material

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>7.91</td>
</tr>
<tr>
<td>Ash content</td>
<td>22.09</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>21.82</td>
</tr>
<tr>
<td>Fixed carbon content</td>
<td>48.18</td>
</tr>
</tbody>
</table>

### Table 2: Surface properties of the treated adsorbents

<table>
<thead>
<tr>
<th>Variables</th>
<th>Adsorbent (ferric oxide treated)</th>
<th>Adsorbent (nitric acid treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>25.2000</td>
<td>19.8000</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.00127</td>
<td>0.00666</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>106.3100</td>
<td>109.8500</td>
</tr>
</tbody>
</table>
The peak formed at 1581.63 and 1579.70 cm\(^{-1}\) signifies the N-H bond formed in the adsorbent material (Shirani et al., 2014) and the band at 1597 cm\(^{-1}\) is from the C=C stretching of polyaromatic C = C peak (Park et al., 2010).

**SEM and EDX analysis of the adsorbent**: SEM is a well-known tool used for investigating the morphology and surface characterization of the material (Sathishkumar et al., 2007). It is also used to study other aspects such as shape, porous nature and the size
Fig. 4: FTIR analysis of the adsorbent treated with nitric acid after adsorption

Fig. 5: SEM image of the adsorbent treated with ferric oxide before adsorption

Fig. 6: SEM image of the adsorbent treated with ferric oxide after adsorption

Fig. 7: SEM image of the adsorbent treated with nitric acid before adsorption

Fig. 8: SEM image of the adsorbent treated with nitric acid after adsorption

distribution of the molecules (Achak et al., 2009). The surface morphological images of the adsorbent treated with ferric oxide solution and nitric acid solution are represented in Fig. 5-8.

It was found from the morphological images that the adsorbents treated with ferric oxide and nitric acid were having different sized pores which will be beneficial for the adsorption process (Hameed, 2009). It was also observed that the adsorbent particles were irregularly shaped in the porous structure. After the adsorption process a notable change in the adsorbent surface was observed. It was found that the surface was heterogeneous in nature signifying that the adsorbent pores were occupied with pollutant molecules (Achak et al., 2009; Arami et al., 2005).

Energy-Dispersive X-ray spectroscopy (EDX) analysis was performed to detect the presence of metal ions on the surface of adsorbent (Werkneh et al., 2018). The EDX analysis of the adsorbents before and after the adsorption of the pollutants are shown in Fig. 9-12. The EDX analysis of the adsorbents before adsorption shows various peaks for the metal ions such as Ca\(^+\), K\(^+\), Mg\(^+\),
Adsorption isotherm: The adsorption isotherm gives the description to understand how the adsorbate molecules distributes on the surface of the adsorbent and the affinity of the solute to the adsorbent at equilibrium (Verma and Sarkar, 2018). It also explains the interaction behavior of the adsorbent and the solute molecule (Zhou et al., 2017). Different isotherm models available from the literature for used for isotherm studies. The prominent isotherm models like Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R) and Flory-Huggins isotherm models were employed to evaluate the mechanism of adsorption.

Langmuir isotherm: The model is obtained by assuming that the adsorbent has active sites distributed uniformly all over the surface and the binding sites are limited (Liu et al., 2010). It explains that once the active site is occupied by the pollutant molecule, the intermolecular forces decreases and there is no provision for the other solute molecule to adsorb on the surface resulting in monolayer adsorption (Mohammad-Rezaei and Jaymand, 2019).

The model also states that the energy of sorption on each of the active sites is uniform (Babaei et al., 2018). The model is given in the simplified form as:

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{max}} + \frac{1}{k_{L} q_{max}}$$

Where:
- $q_{max}$ (mg/g) = The maximum adsorption capacity
- $k_{L}$ (L/mg) = The constant related to affinity of the pollutant to the adsorbent
- $q_{eq}$ (mg/g) = The adsorption capacity and solute concentration at equilibrium conditions
- $C_{eq}$ (mg/L) = Concentration of the dye solution at equilibrium

Mn$^{2+}$, Fe$^{3+}$, P$^{5+}$ which were found to be present as plant nutrients in the tea fibre waste. After the adsorption clear peaks were obtained for the metal ions such as Cd$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ on the adsorbent. This signifies that the metal ions were adsorbed onto the adsorbent surface through the ion exchange process (Iqbal et al., 2009; Lu et al., 2013).
The model parameters are obtained by plotting $\frac{C_{eq}}{q_{eq}}$ against $C_{eq}$.

**Freundlich isotherm:** The model can be applied to adsorption processes which occurs on the heterogeneous surface and the energy distribution is not uniform. The solute molecules gets occupied on the solid surface in form of multilayers (Park et al., 2010). It also, shows exponential decrease of adsorption energy with the coverage on the binding sites (Sarkar and Acharya, 2006). The equation is represented in the linear form as:

$$\log q_{eq} = \log k_f + \frac{1}{n} \log C_{eq}$$  \hspace{1cm} (2)

$k_f$, the Freundlich constant and $n$ denotes the adsorption intensity. The value of $n$>1 signifies that the adsorption is favourable and better interaction of the adsorbate to the adsorbent surface (Bozorgi et al., 2018; Li et al., 2009; Liu et al., 2019). The model constants are evaluated from the plot of $\log q_{eq}$ v/s $\log C_{eq}$.

**Temkin isotherm:** The isotherm model takes into the interactions between the solute and the adsorbent molecule during the adsorption process. It also suggests that the adsorption energy of the molecules in the various layers decreases linearly as the solute molecules are occupied on the active sites (Yousef et al., 2011). It is represented as:

$$q_{eq} = B_T \ln A_T + B_T \ln C_{eq}$$ \hspace{1cm} (3)

$A_T$ (L/mg) the model parameters and $B_T$ (J/mmol) the constant related to heat of sorption. The parameters are evaluated by plotting $q_{eq}$ v/s $\ln C_{eq}$.

**Flory-Huggins model:** The Flory-Huggins (FH) model is employed for studying the extent of surface coverage characteristics of the pollutant on the solid surface and it describes the feasibility of the adsorption process (Foo and Hameed, 2010). It is written in the simplified form as:

$$\log(\frac{\theta_s}{C_s}) = \log k_n + n_a \log(1 - \theta_s)$$ \hspace{1cm} (4)

$k_n$, equilibrium constant, $n_a$ model constant $\theta_s$, the surface coverage value is obtained by:

$$\theta_s = 1 - \frac{C_m}{C_s}$$ \hspace{1cm} (5)

**Dubinin-Radushkevich model:** The Dubinin-Radushkevich (D-R) model is helpful in evaluating the apparent free energy of adsorption and is represented as (Kilic et al., 2011; Rathinam et al., 2019)

$$q_{eq} = q_{ad} e^{-\beta \varepsilon}$$ \hspace{1cm} (6)

$\beta$ the sorption energy constant (mol)$^2$/kJ$^2$, $q_{ad}$ the D-R capacity (mg/g) and by plotting $\ln q_{eq}$ v/s $\varepsilon^2$ the model constants $\beta$ and $q_{ad}$ are obtained. $\varepsilon$ the Polanyi potential which is calculated using:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_{eq}}\right)$$ \hspace{1cm} (7)

The mean free energy is obtained using the formula:

$$E = \frac{1}{\sqrt{2 \times \beta}}$$ \hspace{1cm} (8)

The factor $E$(kJ/mol) shows the energy required to transfer 1 mol of the solute to the adsorbent surface from infinity in the solution (Omidinasab et al., 2018). The values of $E$ between 8 and 16 kJ/mol shows that the process is chemical adsorption and the $E$ value lower than 8 kJ/mol signifies the interaction mechanism is physical in nature (Kumar et al., 2018; Omidinasab et al., 2018).

The isotherm experiments were conducted in the concentration ranges of 5, 10, 15, 20 and 25 mg/L for various metal ions. The different isotherm models were investigated with respect to single component equilibrium data. The calculated model parameters with the obtained regression coefficient values for iron treated and nitric acid treated adsorbents are given Table 3-6. The results obtained showed that Freundlich model fits better with the experimental data and it signified that adsorption of the solute on the adsorbent is physical and it takes place in multilayers. The Langmuir constant $k_l$ was evaluated which shows the affinity of solute molecules to the adsorbent (Verma and Sarkar, 2018). The values of the monolayer adsorption capacities obtained from the Langmuir model are represented in Table 3. The adsorption intensity $n$ shows the types of process. The value of $n$>1 indicates that the adsorption is physical in nature. The process is chemical in nature if the values of $n$ is <1. Thus, from the obtained values of $n$ it can be inferred that the accumulation of the pollutant...
Table 3: The Langmuir model parameters obtained for both the adsorbents

<table>
<thead>
<tr>
<th>Elements</th>
<th>adsorbent (ferric oxide treated)</th>
<th></th>
<th></th>
<th>adsorbent (nitric acid treated)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( k_L ) (L/mg)</td>
<td>( R^2 )</td>
<td>( q_m ) (mg/g)</td>
<td>( k_L ) (L/mg)</td>
</tr>
<tr>
<td>Cd</td>
<td>31.010</td>
<td>1.82217</td>
<td>0.7938</td>
<td>29.130</td>
<td>1.6982</td>
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<tr>
<td>Zn</td>
<td>18.810</td>
<td>0.4207</td>
<td>0.8264</td>
<td>13.482</td>
<td>1.5714</td>
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<tr>
<td>Ni</td>
<td>13.280</td>
<td>1.0561</td>
<td>0.76508</td>
<td>99.120</td>
<td>0.2643</td>
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<tr>
<td>Cu</td>
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<td>0.7040</td>
<td>0.8056</td>
<td>11.140</td>
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<tr>
<td>Pb</td>
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<td>0.2130</td>
<td>0.8319</td>
<td>15.330</td>
<td>0.4511</td>
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Table 4: Freundlich model constants determined from the experiments

<table>
<thead>
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<th>Adsorbent (nitric acid treated)</th>
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</thead>
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<tr>
<td></td>
<td>( k_f ) (mg/(L)(1/n))</td>
<td>( n )</td>
</tr>
<tr>
<td>Cd</td>
<td>1.8892</td>
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</tr>
<tr>
<td>Zn</td>
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<td>5.100</td>
</tr>
<tr>
<td>Ni</td>
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<td>3.6307</td>
</tr>
<tr>
<td>Cu</td>
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<td>9.0320</td>
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<tr>
<td>Pb</td>
<td>1.7262</td>
<td>5.9937</td>
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Table 5: Flory-Huggins model parameters obtained from the experiments

<table>
<thead>
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<th>Elements</th>
<th>Adsorbent (ferric oxide treated)</th>
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<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( k_0 )</td>
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<tr>
<td>Cd</td>
<td>0.8715</td>
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<tr>
<td>Zn</td>
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<td>Cu</td>
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<tr>
<td>Pb</td>
<td>1.4154</td>
<td>0.5609</td>
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Table 6: Temkin model constants determined from the experiments

<table>
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<th>Adsorbent (ferric oxide treated)</th>
<th>Adsorbent (nitric acid treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_T ) (L/mg)</td>
<td>( B_T ) (L/mol)</td>
</tr>
<tr>
<td>Cd</td>
<td>27.48</td>
<td>8.9133</td>
</tr>
<tr>
<td>Zn</td>
<td>5.524</td>
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<tr>
<td>Ni</td>
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<tr>
<td>Cu</td>
<td>3.3717</td>
<td>1.2255</td>
</tr>
<tr>
<td>Pb</td>
<td>18.978</td>
<td>6.738</td>
</tr>
</tbody>
</table>

on the solid surface is physical in nature (Singh et al., 2018). The \( A_T \) value obtained was highest for cadmium ion for both the Fe treated and nitric acid treated adsorbent signifying that the cadmium was adsorbed onto the adsorbent surface to the maximum extent compared to the rest of the metal ions (Ray et al., 2018). The free energy factor E obtained from D-R Model are shown in Table 7. From the values of E which are lower than 8 kJ/mol, it can be concluded that the adsorption process follows physical type (Kumar et al., 2018).

Interaction mechanism between the pollutants in the solution during adsorption: The pollutant molecules present in the multicomponent solution interacts with each other for the active sites present on the adsorbent surface. The mechanism can be found by comparing the adsorption capacity values of the component (i) in the single component mode \( q_i \) and the capacity of the same component (i) in the multicomponent solution \( q_{i,m} \). The different interactions between the adsorbate and adsorbent are:

2018a; Li et al., 2013). The iron treated adsorbent possesses better stability over a long period of time. Various functional groups attached on the adsorbent surface have improved chemical bonding with the adsorbate and the pores present provide larger space for the accommodation of the pollutants (Rule et al., 2014; Zhou et al., 2017). The adsorbent treated with ferric oxide has also advantages that it has high density active sites and larger surface defects which are beneficial for the adsorption (Siddiqui and Chaudhry 2017).

Nitric acid will also have similar influence on the properties of the adsorbent by changing the surface and texture of the material (Hosseini and Hosseini-Bandegharaei 2011; Li et al., 2012). But the above treated adsorbent may not be effective in retaining the chemical species in the pores compared to the adsorbent treated with ferric oxide.

It can be observed from Table 3 that the adsorption capacity of cadmium was maximum compared to other metal ions. This is because of the reasons such as high affinity of the solute towards the adsorbent, ionic properties, electronegativity, covalent index and hydration free energy (Bozorgi et al., 2018; Terdputtakan et al., 2017). In the multicomponent solution lead is another metal which shows the better results next to cadmium. The properties such as ionic radius, ionic potential and hydration energy of lead are very much suitable in forming the metal adsorbent complex which facilitates adsorption. (Erci et al., 2010; Liu et al., 2019; Loganathan et al., 2018).

The other pollutants zinc, nickel and copper also showed their promising values of adsorption capacity. The possible reasons for these outcomes are size of the solute molecules, its binding energy required for interaction, association with the functional groups present on the adsorbent surface, the type of forces possible between the solute-adsorbent and affinity with the adsorbent surface (Erto et al., 2015; Nashtifan et al., 2017; Zeledon-Toruno et al., 2005) (Table 7).
Table 7: Dubinin-Radushkevich model parameters calculated for both the adsorbents

<table>
<thead>
<tr>
<th>Elements</th>
<th>qe (mg/g)</th>
<th>β (mold^-2 K^-2)</th>
<th>EkJ/mol</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
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<td>1.3E-3</td>
<td>0.196</td>
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<td>2.1E-6</td>
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<td>Cu</td>
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<td>Pb</td>
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<td>5.2E-6</td>
<td>0.310</td>
<td>0.6708</td>
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<tr>
<th>Elements</th>
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<th>β (mold^-2 K^-2)</th>
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<tr>
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<tr>
<td>Pb</td>
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<td>6.9E-6</td>
<td>0.2269</td>
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</table>

Table 8: The adsorption capacity of the components in single solution and multicomponent solutions and the interaction effect between the pollutants

<table>
<thead>
<tr>
<th>Elements</th>
<th>qe_j,m mg/g</th>
<th>qe_j,m mg/g</th>
<th>qe_j,m/qe_j,</th>
<th>Interaction effect</th>
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<td>Cd</td>
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<tr>
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<td>Synergism</td>
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<td>25.344</td>
<td>1.1499</td>
<td>Synergism</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>qe_j,m mg/g</th>
<th>qe_j,m mg/g</th>
<th>qe_j,m/qe_j,</th>
<th>Interaction effect</th>
</tr>
</thead>
<tbody>
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<tr>
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<tr>
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<td>Synergism</td>
</tr>
</tbody>
</table>

Synergism: The adsorption capacity of a component enhances because of the existence of other components in the solution (qe_j,m > qe_j).

Antagonistic interaction: The adsorption capacity of a component is suppressed due to the presence of other solute molecules in the solution (qe_j,m < qe_j).

Non interaction effect: The adsorption capacity of a component is not effected by the presence of the other components in the system (qe_j,m = qe_j) (Singh et al., 2018; Terciputtakum et al., 2017).

The interaction effect for the overall system can also be found by comparing the total adsorption capacity of all the components in the single solution mode (Σq_i,j) and in the multicomponent solution (Σq_i,j, m) which are found as using:

\[ \sum_{j=1}^{m} q_{i,j} = q_{i,m} + q_{i,m} + q_{i,m} + \ldots \quad (9) \]

\[ \sum_{j=1}^{m} q_{i,j,m} = q_{i,m} + q_{i,m} + q_{i,m} + \ldots \quad (10) \]

The system shows synergistic interaction as the value of (Σq_i,j, m) > Σq_i,j > (Σq_i,j). But antagonistic behavior is observed if the value of (Σq_i,j, m) < (Σq_i,j). (Bohï, et al., 2017; Hameed et al., 2008).

Interaction effects in the multicomponent solution: The calculated adsorption capacities of the components in the single solution and multicomponent solution mode for both ferric oxide treated solution and nitric acid solution are shown in Table 8. It was observed that the total the total adsorption capacity:

\[ \sum_{j=1}^{m} q_{i,j} \]

For the combined system was more than the total adsorption capacity:

\[ \sum_{j=1}^{m} q_{i,j,m} \]

In the single solution mode which exhibits synergistic type of behaviour. The possible reason for the above interaction is because of the adsorbate such as molecular polarity, reduction potential, ionic size, molecular weight and the surface properties and the structure of the adsorbent and the functional groups present on the surface (He et al., 2018b; Lu et al., 2013; Wang et al., 2019).

CONCLUSION

The tea fiber waste was used effectively as an adsorbent for removing the pollutants cadmium, nickel, zinc, copper and lead from wastewater. The surface properties of the adsorbent were enhanced by treating the material with ferric oxide and nitric acid. From the FTIR and SEM analysis the functional groups on the adsorbent surface were detected and the surface morphology was studied. The isotherm data were fitting best with the Freundlich model signifying that adsorption process is
physical in nature and takes place in multilayers. The existence of physical type of adsorption was also supported by the values of n and E. The multicomponent studies resulted in synergistic types of behavior for cadmium, zinc and lead and antagonistic nature for nickel and copper. The maximum adsorption capacity values obtained for different metals were promising. Finally, it is concluded that the tea fiber waste is efficient for the preparation of the adsorbent and for removing toxic metals from wastewater.

ACKNOWLEDGEMENT

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REFERENCES


