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Ferrite Nanocomposite (Rice Straw-$CoFe_2O_4$) as New Chemical Modified of for Treatment of Heavy Metal from Waste Water

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Abstract

The agricultural by-products such as Rice Straw (RS) has widely investigated as an efficient alternative for current costly methods of removing heavy metals from waste water. RS were modified by $CoFe_2O_4$, results of adsorption indicated that RS treated with $CoFe_2O_4$ spinel ferrite nanoparticles appeared to be more efficient to remove heavy metals from waste water. Where the percentage removal of Fe, Mn, are 84.25%, 92.45% respectly and Cu, Cd, Zn, Ni, Pb are 100% removal. The prepared samples were characterized using different analytical techniques, X-ray diffraction (XRD), FTIR, Transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Atomic Absorption Spectrometer (AAS) using in determination of concentrations of heavy metals.

Keywords: Rice Straw (RS); Cobalt ferrite nanoparticles; Agricultural waste; Waste water treatment

Introduction

Water Pollution defined as Change of chemical, physical and biological properties of water which restricts its use in the various applications [1]. The effluents no disperse in water systems and so change water quality has happen. The contamination of heavy metal in waste water streams from various industries such as wire drawing, printed circuit boards, metallic coatings, mining and agricultural sources where fertilizers and fungicides are widely using [2]. Lignocelluloses one of the malignant wastes in the world is Rice Straw. Before wheat and maize, the most third important grain crop in the world production is rice. Chemical composition of Rice Straw contains lignin (5-24%), hemicellulose (19-27%) and cellulose (32-47%) [3]. Phenomenon of black cloud is released when Rice Straw burning, affecting on human health, visibility, and global climate by emitting gaseous pollutants. binding sites of rice straw able remove metal on aqueous solution by adsorption like activated carbon [4]. On the surface of rice straw have functional groups, binding characteristic may tack up metals from waste water. Rice straw advantage with low-cost bio-adsorbent in removal heavy metals from water and waste water [5].

Large ratios between surface and volume of fabrication of nonmaterial is very important in treatment of pollutants. Nanotechnology have role in our environment, by production new materials, sensors and treatment techniques for monitoring purposes [6]. The contaminants removal from the environment is occurred so rapidly, efficiently and within low costs framework. Thus, the novel nanomaterial field in Nanotechnology with increased affinity, selectivity and capacity for heavy metals. The nanoparticles (NPs) are ultra-fine particles in the size of nanometre order. In many cases, the particles from 1 to 100 nm are generally called as nano particles. The nano sized magnetic materials show many novel properties, especially, magnetisation behavior different than bulk magnetic material. Recently, the use of nano-sized magnetic material as adsorbents has happen increasing interest due to their high surface area and unique super paramagnetism. These properties lead to high adsorption efficiency and high removal rate of contaminants [7]. The stability of magnetic nanoparticles is utmost important for their applications. This can be greatly improved by preventing their oxidation and aggregation. Modification of the surface of magnetic nanoparticles by attaching organic or inorganic materials is proven to be greatly enhances the stability and prevents aggregation. Further these attached groups have specially function group that can ion selective uptake [8].

Magnetic oxides, such as Fe_3O_4, acting as adsorbents (nano) to removal of many metal ions from waste water, such as Ni^{2+}, Cu^{2+}, Co^{2+} and Pb^{2+}. the mainly properties of Magnetic nanoparticles are large surface /volume ratio, bind with chemicals and then they be removed using a magnet. In water problems, nanotechnology of nanoparticles is useful for treatment of water contaminants including bacteria, viruses, and heavy metals like, Nickel, chromium, etc. [9]. Cobalt ferrites one subject of researchers interests due to its high saturation magnetization and coactivity. Cobalt ferrite materials are known to exhibit very high cubic magneto crystalline anisotropy. The magnetic properties of the Cobalt ferrites are very good are known to be mainly attributed to the Co ions in a spinal lattice [10]. Cobalt ferrite ($CoFe_2O_4$) belongs to opposite spinel structure in which half of Fe^{3+} ions occupy tetrahedral sites and the other half occupy the octahedral sites with Co^{2+} ions. In the inverse spinel structure the magnetic moment of Fe^{3+} in the tetrahedral sites is aligned in opposite direction to that of Fe^{3+} in the octahedral sites and hence the net magnetic moment produced from Fe^{3+} is zero. So the net magnetic moment of $CoFe_2O_4$ is due to the magnetic moment of Co^{2+} in the octahedral sites [11]. Many synthetic methods to prepare highly crystalline and uniformly sized magnetic nanoparticles of Cobalt-Ferrites have been studied such as the precipitation method [12]. The solvo thermal method [13]. the co-precipitation method [12], the hydrothermal method [14] and the sol-gel method [15]. Sol-gel is a simple way to produce ultra-fine powders due to their simple synthesis equipment and process. The reason behind studying and opting for this sol-gel route is that the reactants used for the process are cost effective, safe and environmentally friendly [16]. Adsorption capacities of native plant materials usually show lower maximum. Nevertheless, these capacities can be significantly increased with a suitable method such as treatment with various hydroxides, acids; carbonization and hydrolysis have been reported recently. Combination of nonmagnetic powdered material with magnetic nano or microparticles results in a formation of magnetically responsive (bio) composites which exhibit response to external magnetic field [17].

Methodology

Preparation of adsorbent materials

Rice Straw (RS): By-product Straw remained after Rice being harvested was gathered from local market.

1. Washed well to remove water soluble and dirt substances via soaking suitable amount of RS into a detergent solution for 50 minutes, followed by extensive washing 4-5 times with tap water for 1 hour and left till next day in tab water, finally washed with de-ionized water and squeezed.
2. RS cut to small pieces, dried in oven at 65°C to 2 hours (constant weight). For preservation, RS kept in plastic bags and preserved in desiccators until the time of use to minimize contact with humidity [18].
3. The Raw RS was characterized using different techniques such as FTIR and SEM.

Synthesis of cobalt- ferrites nanoparticles

The process for synthesis of mono disperse $CoFe_2O_4$ with super paramagnetic behavior at room temperature was carried out as following:

1. 10.8 g of $FeCl_3.6H_2O$ (MW 270.32) was mixed with 3.3 g of $Co Cl_2.2H_2O$ (M.W 165.9) and dissolved in 50 ml de-ionized water (2:1 molar ratio) according to the stoichiometric proportion of Co and Fe in $CoFe_2O_4$. 1.28 g of Citric acid (M.W 192.124) was added as gelling agent (3:1 molar ratio).
2. 4M ammonia solution (NH_4OH) was added in order to keep the pH of the solution to 7.0 with continuous stirring using a magnetic stirrer.
3. Continuous stirring for 9 hours at 85°C, the clear sol. was completely turned to a gel.
4. Dried in oven at 80°C till constant weight and grinded to fine powder, the powder was calcined at 550°C for 5 hours in furnace under air atmosphere [10].

Preparation of RS-$CoFe_2O_4$ ferrite nanocomposite

For increasing adsorption capacities of adsorbent use RS in modified form.

1. 5 g of RS was added to 0.5 g of Cobalt- Iron Oxide nanoparticles.
2. Refluxed with 30 ml Ethyl Alcohol and 30 ml NaOH (2.5%) at 85°C for 3 hours.
3. Filtrated and washed for several times with HCl (0.1 N) then by deionized water. Then, the modified RS was dried at 105°C till constant weight [19]. A photograph of prepared RS-$CoFe_2O_4$ nanocomposite was shown in Figure 1. where RS/$CoFe_2O_4$ Nanocomposite used in the adsorption study was characterized by using FTIR and SEM.

Figure 1: Prepared RS-$CoFe_2O_4$ Nanocomposite.

Characterization methods and instruments

The FTIR, XDR, SEM, TEM, AAS analyzed at the analytical Laboratory, The City of Scientific Research and Technological Applications (SRTA-City), Borg Al Arab, Egypt using Bruker Tensor 37 FT/IR, LabX XRD-6100 shimadzu, JEOL JSM-6360LA, FEI TECNAI SPIRIT, PerkinElmer (PinAAcle 900 T respectably)

Method of treatment (removal of heavy metals): The sewage water samples were collected from Zarkon drain El-Mahmodya Station, Beheria Government, Egypt. Where some Precautions taken:

1. The samples were transferred to laboratory in closed bottles.
2. Distributed in sixteen 2-liter beakers, each of them had 1-liter water volume. Beakers were subdivided into 4 treatments with each adsorbent for 24 hour and 4 treatments with each adsorbent for 72 hours.
3. Adsorbent weight (1 to 4 g) mixed with polluted water (sewage water) to investigate the effect of adsorbent weight on removal efficiencies of different investigated metals and contact time (24 hour to 72 hour) to investigate the effect of contact period on removal efficiencies of different investigated metals.
4. Samples were placed in a shaker for 24 hour or 72 hours at 120 rpm at room temperature [20]. Adsorption was performed for initial heavy metal concentrations of 1.9 and 1.0 mg/L for Fe, 0.53 and 0.3 mg/L for Mn, 0.013 and 0.015 mg/L for Cu, 0.01 and 0.008 mg/L for Cd, 0.18 and 0.1 mg/L for Zn, 0.12 and 0.1 mg/L for Ni as well as 0.163 and 0.1 mg/L for Pb. Metal ions remaining in aqueous solution were determined by AAS. The amount of metal ion adsorbed was calculated as: % Adsorption=((Ci-Cf)/Ci) × 100.

Where Ci: initial concentration and Cf: final concentrate of the metal ions in the solution (mg/L).

Desorption and reusability: Nanocomposites (RS/$CoFe_2O_4$) are undergoing under several investigate as reusability of the adsorbent, regeneration and desorption. Adsorbent (RS/$CoFe_2O_4$) was separated from adsorption process is performed into process which include:

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1. To remove any un adsorbed metal ions, washing with de -ionized water.
2. Mixing resultant metal-loaded adsorbent with 20 mL of 0.10 M HNO_3.
3. Stripping agent in water shaker bath for one hour.
4. The drying adsorbent.

These process was repeated three times [21].

Results and Discussion

Characterization of biosorbent

FTIR of RS before and after treatment: Figure 2 shows the FT-IR spectra of RS-$CoFe_2O_4$ Ferrite Nano particles Composite. terms of intensity of the bands and disappearance of bands after treatment. However, slight changes were found for some functional groups. For instance, Broad absorption band at 3436 cm^{-1} became broader in Figure 1 and shifted to a lower wave number value 3171 cm^{-1}. Also, strong sharp beaks appeared at 1625 cm^{-1} and 1404 cm^{-1}. Absorbt on band appear at 642 cm^{-1} which belongs to the stretching vibration of the metal-oxygen. The difference indicated that the structure of RS was changed after treatment which indicate the successful modification process.

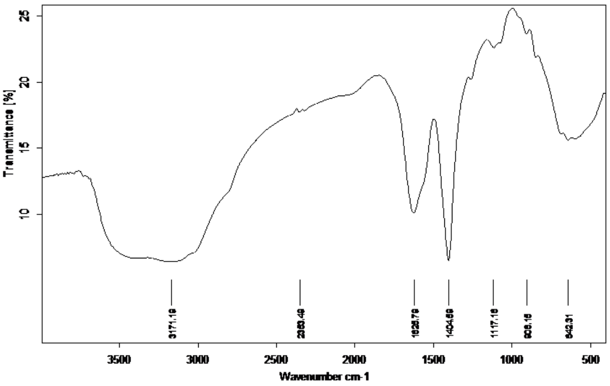

Figure 2: FTIR for RS- $CoFe_2O_4$ nanocomposite (modified RS).

XRD: Figure 3 shows the X-ray diffraction pattern of the calcinated cobalt ferrite nanoparticles. This pattern matches well with the standard diffraction data of $CoFe_2O_4$ crystals. Using XRD, it is confirmed that the samples were cubic structure in nature. All peaks of the prepared sample and its position at 2θ scale are completely compatible with the characteristic peaks of cubic spinel $CoFe_2O_4$ and they are matched with the XRD card no.22-1086. The $CoFe_2O_4$ peaks are particularly sharp. Other oxides or impurity phases are not detected which indicate that we have pure cubic spinel $CoFe_2O_4$ [16].

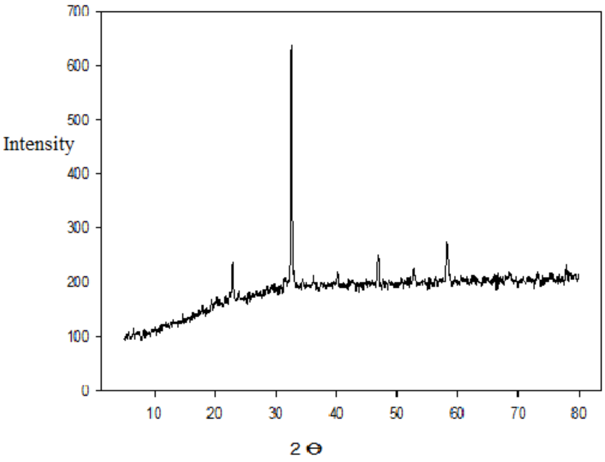

Figure 3: XRD pattern for $CoFe_2O_4$ Nanoparticles.

TEM: The TEM analysis presented in Figure 4 reveals mildly agglomerate pseudo spherical particles with a grain size ranging between 42.9-86.7 nm. TEM imaging has permitted the precise view regarding the size and shape of theobtained particles. Particles have two shapes; common one is spherical and elongated as shown in the TEM images.

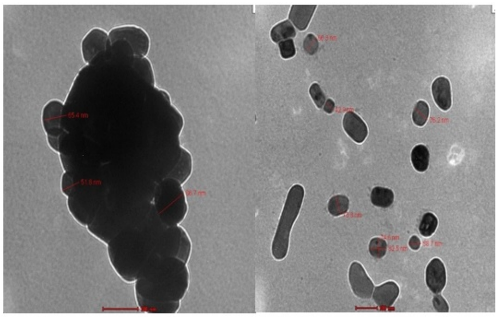

Figure 4: TEM images of the $CoFe_2O_4$ nanoparticles at a scale of 100 nm.

SEM: Figure 5 shows the SEM images of RS -$CoFe_2O_4$ nanocomposite. SEM images show that the $CoFe_2O_4$ nanoparticles are presented on the surface of RS.

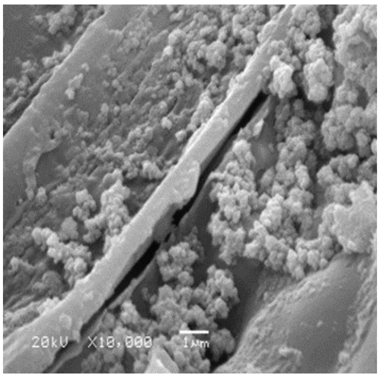

Figure 5: SEM images of RS- $CoFe_2O_4$ nanocomposite.

Removal efficiencies of heavy metals by using raw rice straw

Concentrations of different investigated metals such as Fe, Mn, Cu, Cd, Zn, Ni and Pb were measured in sewage water samples before and after being treated with different dosages of RS. Also, different retention time 24 and 72 hour. relation between contact time and removal efficiency is linearly proportional [18]. Their removal efficiencies were detected, and the results were as follow in Tables 1 and 2 where: in Table 1 as the weight of adsorbent increase, the heavy metal percentage treated increase at 24 hours. in sample 1 the Fe, Mn, Cu, Cd, Zn, Ni and Pb, are measured, the large heavy metal treated was Ni was 55.29% in weight of adsorbent 4 g in sample 1, when in sample 2 was Zn was 70%, while the least one treated was Fe in sample 1 and 2 were 21.05 and 38.42% respect. As same time Mn, Pb and Zn were half percentage treated.

When removal of metal ions from solution the time of equilibrium is effective factor. Increasing of contact time is accompanied with enhancing of uptake of both metal ions as due to the decreased coefficient of mass transfer for diffusion-controlled reaction between the metal ions and the adsorbent [22]. which indicate in retention time 72 hour, in sample 1 and 2 the large heavy metal treated was Cu was 100% that clear that active dose is 3 g so 4 g become waste. while Fe metal still the least metal treated except if removal percentage increases by retention time increase. The rest of metals have more than half percentage treatment in dose 4 g of rice straw.

Weight of adsorbent (g)		Percentage of removal (%) by Rice straw													
		24 hours							72 Hours						
		Fe	Mn	Cu	Cd	Zn	Ni	Pb	Fe	Mn	Cu	Cd	Zn	Ni	Pb
Sample 1	1	4.1	12.97	23.08	9	26.6	20.63	10.43	6.84	21.58	84.6	14.6	45.56	35	14.78
	2	8.4	23.3	31.77	15	38.5	35.67	18.88	10.53	29.05	92.3	22	53.89	53.23	32.3
	3	15.79	35.79	37.46	28	45.8	50.43	27.54	21.58	47.17	100	50	65.56	72.81	46.93
	4	21.05	40.45	46.15	48	50	55.29	34.6	23.68	48.68	100	80	71.67	75	55.09
Sample 2	1	6.84	15.09	21.22	12	35	28.33	15.52	10.53	26.42	84.6	15	55	45	27.78
	2	11.74	26.42	30.77	21	45.4	41.67	29.86	21.26	33.96	92.3	33	73	63.33	57.3
	3	21.58	47.17	37.56	40	63.8	57.5	40.54	40.53	52.83	100	60	80	75.17	66.93
	4	38.42	50.94	44.45	66	70	65	54.6	48.42	66.04	100	85	84.66	83.33	65.09

Table 1: The percentage removal of heavy metals (Fe, Mn, Cu, Cd, Zn, Ni and Pb) which treated by rice straw.

Removal efficiencies of heavy metals by using modified RS ($CoFe_2O_4$/RS)

In Table 2 use modified RS ($CoFe_2O_4$/RS) with different dose and retention time different to study the percentage removal of heavy metals such as Fe, Mn, Cu, Cd, Zn, Ni and Pb Concentrations of different investigated metals such as Fe, Mn, Cu, Cd, Zn, Ni and Pb were measured in sewage water samples before and after being treated with different dosages of RS. Also, different retention time 24 and 72 hours. relation between contact time and removal efficiency is linearly proportional [18]. Their removal efficiencies were detected, and the results were as follow in Table 2 where: The heavy metal percentage treated increase at 24 hours. in sample 1 measure Fe, Mn, Cu, Cd, Zn, Ni and Pb which indicate that more heavy metal treated were Cu and Cd was 100% in weight of adsorbent 2 g and 4 g in sample 1 and 2, while the least heavy metal treatment percentage was Fe at sample 1 and 2 were 40.45 and 74.1. The rest of metals percentage near to 100%, that indicate the efficiency of $CoFe_2O_4$/RS which appeared in small dose. In retention time 72 hours clear that in weight of adsorbent 4 g all measure element was 100% except Fe and Mn except if they near to 100% (84.25 and 92.45 respectively).

Weight of adsorbent (g)		**Rice Straw-CoFe$_4$O Percentage of removal (%) by Ferrite Nanocomposite**													
		24 hours							**72 hours**						
		Fe	**Mn**	**Cu**	**Cd**	**Zn**	**Ni**	**Pb**	**Fe**	**Mn**	**Cu**	**Cd**	**Zn**	**Ni**	**Pb**
Sample 1	1	12.97	22.45	92.3	58	45.56	35.67	33.7	20.45	30.4	100	100	70	62.5	51. 3
	2	22.45	35.23	100	84.6	53.89	65	56.2	30.58	54.53	100	100	95	85	85
	3	38.58	68.58	100	90	65.56	85	75.8	44.53	73.58	100	100	100	100	91
	4	40.45	70.45	100	100	71.67	89.33	80	51.05	81.05	100	100	100	100	100
Sample 2	1	24.21	32.08	92.3	65	55	41.67	41.1	35.26	33.96	100	100	100	72.5	71.17
	2	41.05	63.58	100	90	73	74.17	73.62	73.68	64.91	100	100	100	95	95.09
	3	73.68	81.13	100	93	80	95.83	95.7	84.21	86.79	100	100	100	100	100
	4	74.1	84.91	100	100	84.66	99.17	99.14	84.25	92.45	100	100	100	100	100

Table 2: The percentage removal of heavy metals (Fe, Mn, Cu, Cd, Zn, Ni and Pb) which treated by CoFe$_2$O$_4$/RS.

Effect of adsorbent weight: The adsorbent weight is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The amount of adsorbent decides the extent of available surface binding sites for adsorption. Hence, the percentage removal of adsorbate increases with adsorbent dosage. The effect of variation of adsorbent amount on the removal of metal ions by raw and modified RS was studied by varing adsorbent amount from (1 to 4 g).

Effect of contact time: The rate of ion sorption is faster of metal ion at initial as cause to large number of available sorption sites for adsorption. For the initial blank surface, adsorption proceeded with a high rate. At the end. The adsorption rate is slower probably due to active sites become saturation and equilibrium is stabilized [23]. The effect of adsorbent weight and contact time on removal efficiencies of heavy metals by RS-CoFe$_2$O$_4$ Ferrite Nanocomposite. In adsorption the most factors have great affect is surface area since with a decrease in particle size is accompanied with more number of binding sites for adsorption. From that mean there are directly relation between Surface area and Adsorption. Waste surface of Agriculture is porous and which contain meso pores, micro pores, and macro pores. Along with volume, area and diameter of pores are also influencing factors. Degree or extent of diffusion is determined by volume and diameter pore for pollutant molecules into the pores. Diffusion is depended on the pore diameter and size of the molecule. If the diameter of adsorbat molecule is smaller than the pore diameter, then the molecule diffuses deeper into the pore. From that finding the surface area is influenced on the number of sorption site [24]. Cellulose of RS can provide binding sites for heavy metals, so it is potential adsorbent for heavy metals when used as adsorbent without Coating the CoFe$_2$O$_4$, but the yield of removal is low and difficult separation of adsorbent from solution. Other site removal of heavy metal with RS-Coating CoFe$_2$O$_4$ nanoparticles is higher yield of heavy metals because of the high surface area to volume ratio of RS-CoFe$_2$O$_4$ nanocomposites [25].

Adsorption mechanism: It can be seen in Figure 6 that the attraction is done between -OH groups (negative charge) of the RS and CoFe$_2$O$_4$ nanoparticles (a partial positive charge) [25]. On the other hand, for adsorption of heavy metal ions by RS/ CoFe$_2$O$_4$ nanocomposite, CoFe$_2$O$_4$ nanoparticles act as a magnet when the metal ions approach to the composite, their surface change from positive charge change to a negative charge they since CoFe$_2$O$_4$ nanoparticles is acted as temporary dipole, it means there will be cationic interaction between CoFe$_2$O$_4$ nanoparticles and metal ions. So, its interaction is physical interaction. The nanoparticles are acted as superior accessible active sites could be the main roles for the higher removal of metal ions by RS/ CoFe$_2$O$_4$ nanocomposite than with raw RS. The nanoparticles are acted as superior accessible active sites could be the main roles for the higher removal of metal ions by RS/ CoFe$_2$O$_4$ nanocomposite than with raw RS. The dispersion of nanoparticles sites on the surface of RS is better which provides more available of adsorption for heavy metal ions. After adsorption, the CoFe$_2$O$_4$ nanoparticles on the surface of RS separated to adsorbent super paramagnetism as magnetic separation [21,26-28].

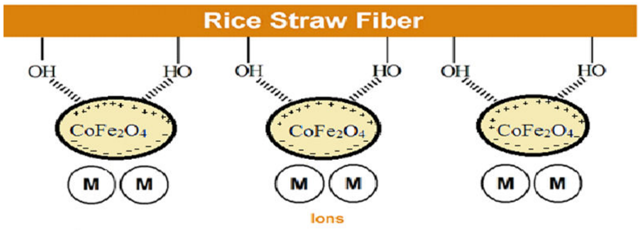

Figure 6: Schematic illustration of adsorption process for heavy metals by RS/ CoFe$_2$O$_4$ nano-composite.

Conclusion

This study shows that the adsorption of metal ions by the modified RS was suitable as compared with the unmodified adsorbent from waste water. Modification of RS with (CoFe$_2$O$_4$) Nanoparticles, and practically use on adsorption ions from waste water, as it gives higher adsorption than unmodified RS. The adsorption study showed that physically attraction between different charges as was responsible for metal ions removal. High surface area of nanoparticles cause to capacity is high of adsorption. The results show RS/CoFe$_2$O$_4$

Nanocomposite is given elimination with highly efficiency for of heavy metal ions as good adsorbent from waste water. From these studies we obtained the optimum conditions for the removal by adsorption mechanism involved mainly is electrostatic attraction as Figure 6.

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