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REMOVAL OF ARSENIC FROM GROUND WATER USING NANO-PARTICLES ADSORBENT

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ABSTRACT:-*Removal of arsenic from ground water was conducted using nano particles cupric oxide adsorbents. Several experiments were performed systematically to optimize the process variables such as adsorbent dose, reaction or contact time, temperature, RPM and pH of water as well as different kinds of impurities present in water and noted their affects on adsorbent process. It was found that cupric oxide (CuO) has very good affinity towards arsenic at ambient temperature and natural water pH with an adsorbent dose of 50 mg per 100 ml of sample having 100 ppb of arsenic level by maintaining maximum permissible limit of competing anions with contact time of 30 minutes stirring speed of 100-150 rpm for uniform distribution of solute in aqua solution for proper reaction. Hence the 100% arsenic removal was achieved by the above cited technique.*

Key words: Arsenic, Nano-particles, Adsorbent.

1. INTRODUCTION

Arsenic, a semimetal/metalloid, is almost present in all the eco-system of the environment. Due to its high toxicity & discreetness, arsenic has been called “The king of Poison” and is described as a human carcinogenic substance of group I by International Agency for Research on Cancer (IARC). Arsenic toxicity causes different types of diseases such as gastrointestinal, cardiovascular, nervous system, damage mucous membranes, mutagenic and skin lesions etc; considering a lot of harmful/powerful effects of arsenic on human life which may able to cause death. The environmental protection authorities have taken a more serious attitude towards the presence of arsenic in water. The scale of the problem of arsenic poisoning is illustrated by the frequently used term “Mass Poisoning”. WHO & EPA re-established a guideline of 0.01 mg/l as the maximum allowable arsenic content, where as Pakistan Standard Quality Control Authority (PSQCA) has recommended MCL of 0.05 mg/l. Arsenic, therefore, is under strict watch globally.

Different techniques and processes have been in practices for the removal of arsenic from ground water so far.

Adsorption processes are also important in the perspective of the present study and are discussed by many researchers developed a house hold unit for removal of arsenic by employing iron coated sand as adsorbent. The system was designed to purify 600-700 liters of treated water with a flow speed of 6.0 liter/hr having arsenic concentration of 0.01 mg/l for an initial arsenic level of 1.0 ppm [1].

Performed experiments with laterite which was a vesieular clay residue found in a large quantity in the tropical regions to remove arsenic from water [2]. Laboratory tests showed its adsorption efficiency which varied between 50 to 90% for 5 gm of laterite per 100 ml arsenic contaminated water under an equilibrium period of 20 minutes. He also modified the process of laterite by treating it with 0.01M nitric acid to raised its adsorption capability by increasing its surface/contact area. He also performed laboratory tests and confirmed that laterite is a best adsorbent for arsenic removal and further proved that the process is an in-expensive removal technique to safe guard the human health by using treated water.

Used only clay from Mymensingh in his study the clay was processed with cellulose organic materials such as de-lignified jute, news paper pulp and saw dust bleached in a solution which is to be acidified with hydrochloric acid or vinegar [3]. Ferric hydroxide coated new paper and pulp adsorbent was used in laboratory scale adsorption filters to remove arsenic by coagulation phenomena. True facts of work, flow and volume showed arsenic removal efficiency equal or less than 0.05 ppm.

Describe the arsenic removal process which consists of filter and arsenic adsorbing tablet [4]. One tablet is enough for 20 liters of water with an efficiency of 95-100% arsenic removal.

Different kind of adsorbents have been developed by researchers in past, these include activated alumina, activated carbon, iron oxides/hydroxides, synthetic zeolites and hydrous titanium dioxide (TiO_2). They are employed for arsenic removal. Consequently upon adsorbents obtained from biological origin, was found also encouraging performance in the arsenic removal technique. No doubt arsenic is a poison for human health, the researcher/scientists and technologist are more and more focused on the improvement and development of old and new methods along with new adsorbents range such as are oxides of metal which are more effective, low cost, and quick to ward arsenic ingestion/removal. Scientists are therefore more concentrated on nano-size adsorbent. Nano-particles are obtained from metal and metal oxides like as titanium oxide [5] metal oxide nano materials [6] cupric oxide [7], nano iron (hydr) oxide impregnated granulated activated carbon, synthetic nano structured Fe(III)-Cr(III), mixed oxide [8].

A brief literature review is available on arsenic removal using nano-particle and still research is going on. According to [7], arsenite As(III) and arsenate As(V) both were adsorb by CuO (cupric oxide) nano-particles very effectively.

In this study arsenic polluted/contaminated water was treated with cupric oxide (CuO) nano-particle as adsorbent. The process parameters like Temperature, stirring speed (RPM), nano-particle adsorbent dose and reaction time/contact time as well as pH behavior of the aqua solution were studies in detail. In this study experiments were also performed on natural water pH, and ambient temp; whereas agitation of mixture is done on minimum rpm for uniform distribution of solute and solvent to reduce the contact time and increase the surface area for proper reaction. The adjustments of these parameters improve the adsorption process more and more effective, inexpensive and applicable for both domestic and commercial application.

2. EXPERIMENTAL SETUP

To optimize the process conditions several experiments were performed by adjusting the adsorbent dosing rate and reactions time. These are the major parameters which directly involved in the adsorption process. Therefore the arsenic removal was observed at different dosing rate such as 5 mg to 60 mg per 100 ml of sample and reaction time was also adjusted for each sample with time limit of 15, 30, 45 and 60 minutes intervals. The other process parameters such as reaction temperature, stirring speed (RPM) and pH behavior of the solution and their effects on the adsorption process and arsenic removal rate were also studies.

The steps involved in the experimental setup are as follows.

Nano Particle Cupric oxide (CuO) which is used as adsorbent in the present study was prepared in the laboratory by the reaction of copper chloride with sodium hydroxide to form copper hydroxide. Allowing it to keep at room temperature for 24 hrs, a precipitate of cupric oxide was produced which was washed with demineralized water, filtered, dried and then grinded to make fine powder. This laboratory prepared nano particles cupric oxide was used in the adsorption process for removal of arsenic.

Arsenic stock solution was prepared by dissolving arsenic trioxide (As_2O_3) salt dried at 105-110 ^oC for one hour then 1.32 gm of it was added in 100 ml of demineralized water containing 4 gm of sodium hydroxide (NaOH) reagent grade salt in one liter measuring flask. Then acidification of the solution was done by adding 20 ml of concentrated nitric acid (HNO_3) and make the volume one liter. The one ml of this stock solution having strength of one mg of arsenic (As).

Arsenic intermediate solution was prepared by dissolving 1.00 ml of arsenic stocks solution in 100 ml of demineralized water containing 1.5 ml concentrated nitric acid (HNO_3) reagent grade and make the volume one liter. The one ml of this intermediate solution having strength of 10 µg of arsenic (As).

Arsenic standard solution was also prepared by diluting 10 ml of intermediate arsenic solution in 100 ml of demineralized water containing 1.5 ml concentrated nitric acid (HNO_3) reagent grade and make the volume one liter. The one ml of this standard solution having strength of one µg of arsenic (As).

Then 0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml of arsenic standard solution were poured in volumetric flask and bring the volume to 100 ml with demineralized water. These solutions having strength of 0, 5, 10, 15, 20 and 25 ppb of arsenic (As) respectively. The 100 ppb arsenic working solution was also prepared by pipetting 10 ml of standard arsenic solution into volumetric flask and brings to volume one liter with demineralized water. Concentration of arsenic (As) 100 ppb per liter was achieved.

Working solution of 100 ppb arsenic concentration samples was prepared in 250 ml conical flask by proper dilution of arsenic stock solution.

A calculated amount of nano particles cupric oxide was added in each sample. The adsorbent dose was adjusted with different dosing rate such as 5 mg per 100 ml to 60 gm per 100 ml of sample.

Conical flask was kept on magnetic stirrer (Mechanical shaker) for proper distribution of mixture. Aqua mixture was agitated for a pre determined time interval of 15, 30, 45 and 60 minutes to obtain the optimum time limit of reaction.

After the completion of reaction, the aqua mixture was filtered and rate of arsenic removal was tested by Merck Arsenic Test Kit (Arsenic Strip Colorimetric Method).

The same procedure was repeated to checked number of samples. The experiments were performed at ambient temperature and natural water pH. The operational parameters that can effect on arsenic removal process are mainly dosing rate, reaction time, stirring speed and presence of competing anions these were adjusted on different rate and studies their affects on the process.

Experiments were performed at Environmental Engineering Laboratory Department of Environmental Sciences, NFC IET Multan. Northern Power Generation Company Ltd (NPGCL)., Thermal Power Station (TPS), Wapda, Muzaffar Garh and Pakistan Council of Research in water Resources (PCRWR) Laboratory in Multan region.

3. RESULT AND DISCUSSION

3.1 Effect of Dosing Rate

The influence of adsorbent rate is one of the most important parameter in the metal oxide adsorption technique. Experiments were performed by adding the calculated amount of adsorbent (CuO) with constant interval of reaction time to calculate the exact dosing rate with maximum removal of arsenic.

Arsenic concentration level of 100 ppb was maintained in a 100 ml of demineralized water sample, a cupric oxide used as adsorbent were injected gradually in to it in the range of 5 mg to 60 mg per 100 ml of sample with contact time of 15 minutes interval and percentage of arsenic removal were observed on each interval of time. The rates of arsenic removal were carried out 40 to 90% with an adsorbent dose of 5 to 60 mg/100 ml of sample and contact time of 15minutes each. The reaction time is not enough to complete the reaction and more contact time is required to complete the reaction or to obtain 100% arsenic removal. Then the same procedure was adopted for 30, 45 and 60 minutes interval of contact time to calculate the optimum values of the adsorbent dose and the contact time. Fig.1 highlighted the rate of adsorption rises with an increase of adsorbent rate; initially the rate of adsorbent is rapid but further reaction rate is increases slowly with an increase of dosing rate up to the maximum limit. Several experiments were performed at different adsorbent dose, finally it was confirmed that the sample containing 100 ppb of arsenic concentration in 100 ml of sample required 50 mg of cupric oxide nano-particles to achieve the 100% removal of arsenic within 30 minutes of reaction time. The consolidated results of contact time and adsorbent dose is summarized as under in Table 1

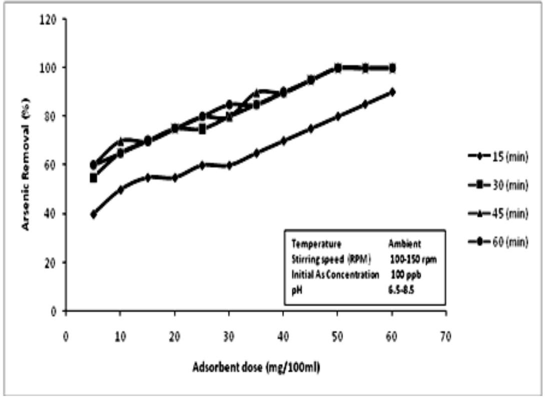

Fig (1):- Profile of removal of arsenic with respect to adsorbent dose

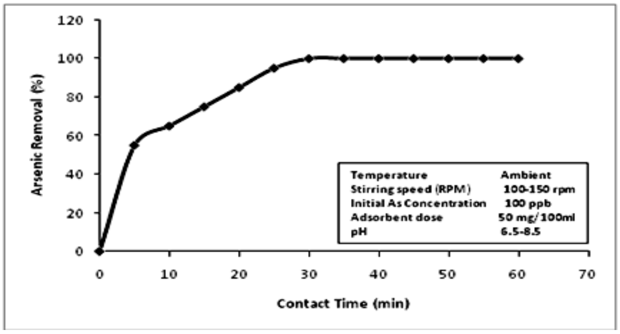

Fig (2):- Contact Time effects on arsenic removal

3.2 Effect of Contact Time

Reaction time has been found as significant parameter in the adsorption process for arsenic removal from arsenic contaminated water. To see this effect, experiments were performed for contact time of 15, 30, 45 & 60 minutes. The initial arsenic concentration of 100 ppb was maintained in 100ml of demineralized water reacted with 50 mg of adsorbent dose of cupric oxide, result is indicated in Fig.2. In the early stage (15 to 20 minutes), the reaction rate became fast and then rate of adsorption decreases to reach at equilibrium within 30 minutes of contact time and 100% removal efficiency was achieved. It was observed that %age removal of arsenic became slowly if arsenic concentrations rise up in the initial stage of the reaction and it will take longer time to complete the reaction. It was very clear that adsorption process is faster in the early stage when arsenic concentration is very low where as reaction become slow for higher concentration of arsenic and removal efficiency may depend on contact time and adsorbent dose.

3.3 Effect of pH

Removal of arsenic from contaminated water is directly depended on process chemistry and pH of the system. Therefore, to study the effect of pH on arsenic removal, Five (5) samples having pH in the range of 2 to 10 with arsenic concentration of 100 ppb/100 ml each were reacted with 50 mg CuO. The trend is presented in Fig. 3

The fig.3 highlights that pH looks like basic factor in the adsorption process that directly affected the process chemistry of the arsenic contaminated water during adsorption process. In acidic nature, the removal of arsenic is less than that of alkaline media as observed in the experimental test performed at different pH range. The arsenic species remain stable in the pH range of 6 to 10; therefore the pH range of the system may be maintained in between the above range. It is economical & inexpensive if the process will continue on the natural water pH. The several experiments were performed on natural water pH and it was observed that there is no noticeable impact on adsorption rate.

3.4 Effect of RPM

Proper agitation of adsorbent is the important characteristics in adsorption process. The reaction time is directly depending on the contact time of solute and solvent. Proper distribution of solute increases the adsorption rate. Experiments performed at three different stirring speeds, i.e. 100, 150 and 200 rpm but there is no significant effect on arsenic removal rate due to change in RPM. It was observed that proper distribution of solute was maintained with proper agitation rate of 100-150 rpm, because the solid (adsorbent) was fully suspended in the solution and adsorption process reached at equilibrium and having no impact of reaction rate with increase in rpm rate. Therefore the rate of agitation should be adjusted within the range of 100-150 rpm.

3.5 Effect of Temperature

With varying temperature from 30^{o}C to 40^{o}C, adsorption rate was enhanced by 3-5%; which is a nominal change in adsorption rate. Therefore it is suggested that the process can be carried out on ambient temperature which is safe, economical & acceptable because 100% removal of arsenic took place with optimum conditions of adsorbent dose, contact time and RPM with natural water pH and ambient temperature conditions.

3.6 Effect of Different Anions Present in Drinking Water Sample

The anions such as sulfates, carbonates, chlorides and nitrates of sodium salts were dissolved homogeneously in above samples separately up to a maximum permissible limit as guided by WHO, to observe their effect on adsorption process by adding a 50 mg of cupric oxide (CuO) adsorbent in all the samples. All the operational parameters such as contact time, RPM, pH, temperature were considered to calculate removal of arsenic from all the samples and results are given in table 2 It was evident that these impurities have no significant effect on the adsorption process.

Table (1):- Impact of adsorbent dose and reaction time

Sr#	Total Arsenic level before reaction (ppb)	Adsorbent dose (mg/100ml) of sample	%age of Arsenic removal (15 mints)	%age of Arsenic removal (30 mints)	%age of Arsenic removal (45 mints)	%age of Arsenic removal (60 mints)
1	100	05.0	40	55	60	60
2	100	10.0	50	65	70	65
3	100	15.0	55	70	70	70
4	100	20.0	55	75	75	75
5	100	25.0	60	75	80	80
6	100	30.0	60	80	80	85
7	100	35.0	65	85	90	85
8	100	40.0	70	90	90	90
9	100	45.0	75	95	95	95
10	100	50.0	80	100	100	100
11	100	55.0	85	100	100	100
12	100	60.0	90	100	100	100

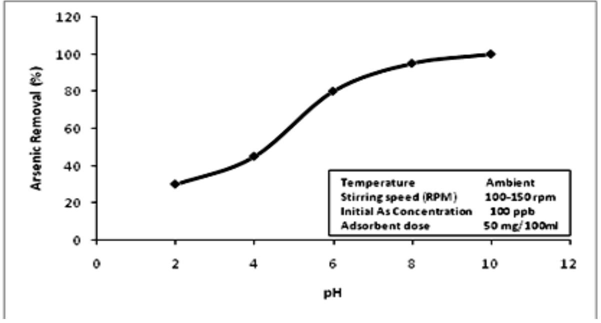

Fig (3):- pH effects on arsenic removal

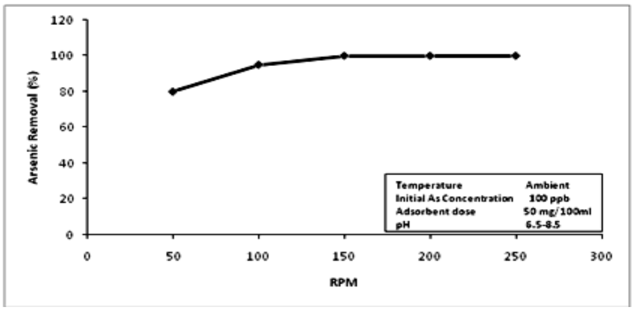

Fig (3.4):- Effect of RPM on Removal of Arsenic

Table (2):- Effect of anions concentration on removal of arsenic

Sr#	Sulfate, Chloride, Carbonate Level Before Reaction (Ppm)	Nitrate Level Before Reaction (Ppm)	Total Arsenic Level Before Reaction (Ppb)	Total Arsenic Level After Reaction (Ppb)	%Age Of Arsenic Removal
1	25	2.5	100	0	100
2	50	3.5	100	0	100
3	100	4.5	100	0	100
4	150	5.5	100	0	100
5	200	7.5	100	0	100
6	250	10.0	100	0	100

4. CONCLUSIONS:-

CuO was found as the best choice. Although its advantage of cheap and readily available, it is also removes the Arsenic maximum level. A dose of 50mg/100ml was the best adsorbent dose used in the study.

If other adsorbents (CaO, MgO) used in the study did not remove the Arsenic effectively however CuO removes along with present of other anions.

Contact time was also found a significant parameter and a 30 min contact time removed the Arsenic efficiently.

pH was also an important parameter because maximum arsenic was removed between the pH limit of (6.5-8.5) i.e. natural water pH.

Temperature was found as insignificant variable in the present study.

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