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Environmental Dilemma of Humic Substances: Being Adsorbents and Being Carcinogens

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***Abstract*—Humic materials can be classified as soluble in high pH, soluble in all pH's, and insoluble in all pH's (IHA). In this study, humic substances in the environment were discussed, and their different environmental contributions, either positive or negative, were investigated. Some humic substances help the water treatment while some others cause carcinogenic matter accumulation in water. This dilemma was discussed with different examples. In the first part of this study, IHA was used as adsorbent in removal of some metals, chemical oxygen demand (COD) and color from water. The results were presented together with literature results. IHA could adsorb various heavy metals in 10 to 300 mg/g capacity interval, while COD removal performance was 2270 mg/g. In the second part of the study, soluble humic matter in natural waters and disinfection by-products (DBP) formation upon chlorination of such waters were discussed. Humic fractions were important precusors of DBP's such as trihalomethanes (THMs) and haloacetic acids (HAAs). Depending on the water resource, the humic substances, THM and HAA formation potentials and types and quantities of the compounds may differ, but all are bioaccumulative and potentially carcinogenic. The study investigated the two different faces of humic substances in the environment.**

***Index Terms*—Adsorption, disinfection by-product, humic acid, treatment.**

I. INTRODUCTION

Constituting approximately 65-75% of the total organic substance in the soil, humic substances are comprised as a result of natural disintegration. They are significant components of soil. They can be found not only in soil, but also in natural waters, river, lake and sea bottom sediments as well as other chemical and biological transformation materials, and even in lignite and coal with oxidized bitumen. With a high molecular weight, despite their variable nature regarding atomic charge, they generally carry negative charge. While existing in soluble fraction (HA) in alkali solutions, some may be insoluble within acidic solutions. Their elementary compositions vary based on their origins and preparation conditions.

Humic substances contain high levels of carbon; and aromatic rings and alkyl chains including a great variety of functional groups (carboxylic and phenolic groups, –COOH, –OH, $–NH_2$ etc.) as their fundamental units. Those functional groups have a highly reactive capacity to compete and to create a complex [1], thus, with this feature; they play a key role in aquatic transformation, transportation, disaggregation and bioactivity of metals [2], [3].

The free radicals which are formed as a result of humic acid-metal interaction have a significant role in creation of metal complexes, bonding of heavy metals, pesticides and herbicides, inactivation of microbial enzymes, hence in environmental detoxification [4]. This ability to create complexes derives from the anionic polyelectrolyte characteristic of their structure [5].

Humic acids play quite opposite parts in environmental issues due to their structural differences and resolution characteristics. There are humic forms which contribute to the creation of pollution and/or hazardous compounds, while some of the humic substances are useful in removal. This study aims to explain this contradiction using different examples.

II. MATERIAL AND METHOD

Dissolved and undissolved forms of humic acids have two different roles in environmental aspect. This study discusses the both situations.

A. Humic Acids as Adsorbents in Treatment

Adsorption is an important application for separating dissolved metals from the environment. Various studies have shown that insoluble humic acids (IHA) obtained from coal are efficient in adsorption as well as common adsorbents such as active carbon, clay etc. Depending on the origin of the coal, the performance of every IHA sample as an adsorbent may vary, since the structure of humic acid also changes. Some of many studies on IHA and metal adsorption are selected to present primarily, considering the metal bonding characteristic of humic acid. The results of the experimental studies which have been performed with IHA which was synthesized from Konya lignite in laboratory conditions shall be evaluated along with the others. The IHA has been synthesized from 2 different kinds of lignite from Konya region (Beysehir and Ermenek), using the method presented in the previous studies [6]. Heavy metal adsorption tests on IHA samples are performed in batch reactor systems. 0.1 g IHA sample has been added to synthetic solutions of different metals, and shaken on 220 rpm to ensure IHA contacts with the solution. The metal concentration has been followed with time. The adsorption capacities have been calculated using the equilibrium concentrations. The efficiency of IHAs in the removal of other important pollution indicators, color and organic matter (COD), has also been demonstrated. This information, when evaluated alongside with other studies on adsorption using IHAs

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obtained from different types of coal, propounds that IHA may be employed as adsorbent in treatment.

B. Humic Acids as Potentially Hazardous Substances on Drinking Water Supply

Surface waters contain natural organic materials (NOM) which are formed as a result of natural decompositions in the ecosystem. Structure and amount of these materials may vary between the sources. Natural organic materials have a potential to transform into hazardous disinfection by-products (DBP) in consequence of chlorination which is a common method of disinfection in drinking water supply. The most common of those products are trihalomethanes (THM), haloacetic acids (HAA) and haloacetonitriles (HAN) [7]. Each of these groups contains different number of components. Within chlorinated water, the type and the amount of these components depend on season, geographical position, the amount and the structure of the natural organic material, bromide concentration, pH, temperature, NOM characteristics and amount, chlorine/bromine rate, SUVA254 etc [8]. Within natural material structure, fulvic and humic fractions are the ones which contribute to the creation of THM most.

It was after the presentation of DBP formation in the literature that those parameters took place in drinking water standards of many developed countries in the world, even the first limit values have been decreased in time. Yet, the issue has taken place in Turkish legislation very recently.

In the second half of this study, characteristics and detrimental effects of NOMs and the factors that affect their formation shall be discussed as well as the literature information about drinking water limit values in Turkey and in the world.

III. ADSORPTION WITH HUMIC ACIDS

A. Adsorption onto IHA

There are many studies about the adsorption of different parameters, such as radioactive materials, organic materials and especially metals, onto IHA which is obtained from soil or various kinds of coal. Some of these shall be discussed in the forthcoming parts. Within the scope of this study, Cr, Zn, Cu, Mn and Fe adsorption from aqueous solutions onto IHA has been demonstrated, using low quality lignite with extended reserve from Konya-Beysehir and Karaman-Ermenek regions to synthesize the IHA with the method explained in previous studies [6] (Fig. 1).

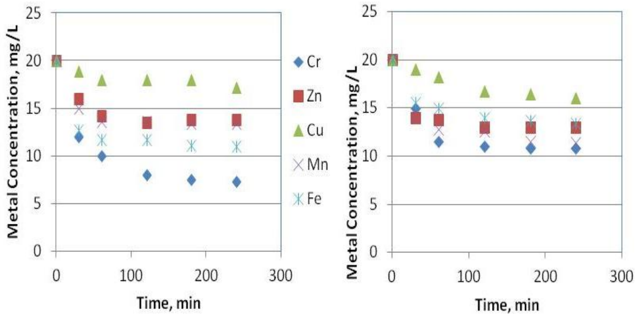

Fig. 1. The change of the residual concentration during Cr, Zn, Cu, Mn ve Fe adsorption onto (a) Beysehir IHA (BIHA) and (b) Ermenek IHA (EIHA).

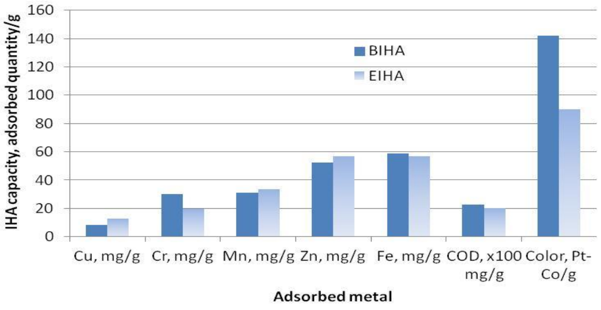

Fig. 2. Comparison of metal, COD and color adsorption capacities of Humic acids.

In the study performed with the initial concentration of 20mg/L, the system has reached the balance between the first 60-120 minutes for all the metals, and no significant metal removal has been observed after that period. It is possible to say that IHA samples have not been highly successful to remove those metals, but still there have been some decreases in metal concentrations.

Fig. 2 shows the comparison of metal, organic material and color removal capacities of two humic acids. Their performances are approximate. IHAs were more successful in color and COD removal than metal removal. In general, 2040-2270 mg/g COD removal and 90-144 Pt-Co/g color removal can be considered as high capacities indicating that these IHA samples can be successively used even in treatment of high COD and high color industrial wastewater. This adsorption kinetic has been analyzed in another study [9]. The main goal in this part of the study is to determine the environmentally useful characteristic and usage of humic acid (IHA) which is insoluble. The adsorbent usage of IHA shall be demonstrated, evaluating the experimental findings together with the studies in the literature performed for different IHA samples as indicated in Table I. The table is a short review of the studies performed with IHAs of various origins, and indicates that, performances vary with the origin of the IHA and adsorbed matter onto it.

B. Another Role of Humic Acid in Adsorption

Metal binding properties of humic acid affects the adsorption performance when it is present in the medium where other adsorbents are adsorbing metals. Three ways of the effects of humic acids in such systems were reported, either positive or negative [18]. As the first effect, metal-humic acid complexes that are not adsorbable are formed. In the second effect humic acid directly bonds onto adsorbent surface and metal adsorption reduces as a result of blocking the adsorption sites on the surface. Whereas in the third effect humic acid forms a bridge between metal and the adsorbent surface, and so increases the adsorption performance [19].

Lai *et al.*, [18] obtained an adsorbent by covering the goethite onto sand particles and and studied the effects of humic acid on Cd adsorption. They found that the addition of humic acid before and after Cd changed the Cd adsorption performance differently. Some studies reported that adsorption capacities of the clays modified with humic acids increased [20], [21]. Adsorption of Cu, Cd and Cr onto Ca-montmorillonite modified with humic acid is higher than non-modified clay, as humic acid changes the adsorption sites onto the surface and so changing the adsorption mechanism and increasing the capacity [20].

IV. POTENTIAL HUMIC ACID HAZARD IN DRINKING WATER

Humic matter content of the surface water is the most contributing factor of DBP formation in drinking water disinfection. Humic matter copmposed of humic and fulvic acids, concentrations of which depends upon the location of water resource, natural vegetation around it, presence of algae and the season of the year [22]. Number of studies have been performed on the DBP formation as a result of reactions of humic and fulvic acids with chlorine [23], [24]. The two common types of DBP's are THM and HAA compounds, they have serious adverse effects on human and environmental health such as cancer as a result of bioaccumulation [25], [26]. Table II indicates some common DBP types and their health effects [27]. Their cancer risks are critical and treatment systems need to be modified to prevent such risks [28].

TABLE I: EXAMPLES OF ADSORPTION STUDIES PERFORMED BY HUMIC ACIDS

Adsorbent	Studied Metals	Result	Reference
Raw and 100 –300 ℃ processed coal	Li, K, Ca, Mg, Ni, Co, Ba, Fe, Zn (with and without alcohol)	Alcohol increased Ni and Co adsorption	Murakami *et al*, 1997 [10]
Humic acids with the COOH groups	Cu, Pb, Mn, Cd	Cu>Pb>Mn=Cd	Manunza *et al*, 1995 [11]
North-Bohemia coal Humic Acid	Cu, Pb, Zn, Ni, Cd, Ca, Mg	0.50, 0.59, 0.18, 0.12, 0.16, 0.1, 0.03 mmol/g	Madronova *et al*, 2001 [12]
Humic Acid	Pb,Ag,Hg,Cd, Ba, Cu, Ni, Co, Mn, Zn, Ca, Mg, V, Al, Cr	Pb>Ag=Hg>Cd=Ba=Cu>Ni= Co=Mn=Zn=Ca>Mg=V=Al=Cr	Martyniuk and Wieckowska, 2003 [13]
Beysehir and Ermenek lignite IHA	Fe(II)	59 mg/g (1.06 mmol/g) for Beysehir IHA and 57 mg/g (1.02 mmol/g) for Ermenek IHA	Tarlan and Ahmetli, 2007 [6]
Humic Acid	Al	acidity, ionic strength, temperature and pH were effective	Wang *et al*, 2007 [14]
Stockton Mine coal Humic Acid	Zn, Cu, and Cd in Acid Mine Drainage (AMD)	for $Ca(OH)_2$ neutralised AMD, addition of lignite derived HS enhanced the removal of Zn, Cu, and Cd	Olds *et al*, 2013[15]
Humin and humic acids isolated from a forest soil in northeast China	adsorption and desorption properties of Cu(II)	humin has a lower adsorption capacity and higher adsorption reversibility for Cu(II). It plays an important role in controlling the fate, transport and bioavailability of Cu(II) in the environment.	Zhang *et al*, 2013[16]
Kaolinite and hematite in the absence and presence of humic acid	Cu(II)	The rate and the amount of adsorption in the absence or the presence of humic acid increased with decreasing ionic strength, increasing pH and in the presence of the background electrolyte K+ rather than Ca2+. Humic acid enhanced the rate and the amount of adsorption	Komy *et al*, 2014[17]
Beysehir and Ermenek lignite IHA	Cr, Fe, Mn, Zn, Cu	Cr:0.49-0.35; Fe:0.25-0.19 Mn:0.24-0.31; Zn:0.19-0.22 Cu:0.09-0.12 meq/g	this study

TABLE II: DBP COMPOUNDS AND HEALTH EFFECTS [27], AND MODIFIED FROM [29]

A. DBP	Cancer Class	*B. Group*	Classification	Description
Chloroform	B2	A	Carcinogenic for human	Epidemiologic studies proved that they are absolutely cause cancer upon exposure
Bromodichlorometane	B2			
Dibromochlorometane	C			
Bromoform	B2			
Dichloroacetic acid	B2	B	Potentially carcinogenic for human	Limited effects according to epidemiologic studies (B1) and/or sufficiently effective according to animal experiments (B2)
Trichloroacetic acid	C			
Dichloroacetonitril	C			
Dibromoacetonitril	C			
2 – Chlorophenol	D	C	Possibly carcinogenic for human	Limited effects were proved by animal experiments but human effects are unknown
2,4 – Dichlorophenol	D			
2,4,6 – Trichlorophenol	B2			
Chloral hydrate	C	D	Not classified	Carcinogenci effects for human and animals are unknown
Formaldehite	B1			
Chlorite	D	E	Not carcinogenic for human	Not carcinogenic as a result of two differnt animal tests or epidemiologic and animal tests
Bromate	B2			
Chlorine dioxide	D			

V. CONCLUSION

In this study, various aspects of humic substances were investigated. In the first aspect, performance of IHAs as adsorbent were presented. Although IHA samples have not been highly successful to remove metals, still there have been adsorption capacities obtained as 35-49 meq/100g for Cr, 19-25 meq/100g for Fe, 24-31 meq/100g for Mn; 19-22 meq/100g for Zn, and 9-12 meq/100g for Cu. Performance of the two studied IHAs at COD and color removal from waters were higher as 2040-2270 mg/g for COD and 90-144 Pt-Co/g for color.

In the second aspect, three alternative mechanisms that humic substances bind metals were described. Formation of non-adsorbable metal-humic acid complexes; direct binding of humic acid onto adsorbent surface, blocking the adsorption sites on the surface and reducing metal adsorption; and third, forming a bridge between metal and the adsorbent surface, and so increasing the adsorption performance.

As the final aspect, the two common types of DBP’s are THM and HAA compounds, they have serious adverse effects on human and environmental health such as cancer as a result of bioaccumulation. Maximum contaminant level (MCL) for total THM concentrations was decreased from 100 to 80 μg/L by USEPA. For HAA compounds, MCL was set as 60 μg/L. Their cancer risks are critical and treatment systems need to be modified to prevent such risks.

Humic substances may either helps to keep the environment, or be the cause of destruction of the life. It depends upon the form, structure, place and the interaction of the substance with its environment. Human have ability to control their potential hazards, and have ability to take their advantages.

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